Adsorption of CO_2 on Indian coals

Thesis submitted

by

BHARADWAJ ADIRAJU (208CH103)

In partial fulfillment for the award of the Degree of Master of Technology

In

Chemical Engineering

Department of Chemical Engineering

National Institute of Technology

Rourkela-769008, Orissa, India

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CERTIFICATE

This is to certify that the thesis entitled, **"ADSORPTION OF CO_2 ON INDIAN COALS"** submitted by Sri BHARADWAJ ADIRAJU in partial fulfillments for the requirements for the award of Master of Technology Degree in Chemical Engineering Department at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date: 03-06-2010

Susmita Mishra
03.06.10

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A. Bharadwaj
03/06/10

Place: Rourkela

Date: 03/06/2010 **(BHARADWAJ ADIRAJU)**

Contents

Abstract

CO_2 sorption studies were conducted for Raniganj coals of India from the point of view of CO_2 adsorption & desorption and the effect of temperature, coal particle size and media pH. Adsorption and desorption studies were conducted for 4 samples with the highest adsorption capacity reported as 11.09mL/g of coal and lowest as 5.15mL/g at 30°C. Desorption studies revealed the existence of both positive and negative hysteresis curves. The minimum desorption capacity was attained for S -2, 1.29ml/g at the pressure of 22.361Psi. Hystresis was minimum for sample 1. While sample 3 and sample 5 showed maximum positive hysteresis. The hysteresis increases with increasing pressure initially and extended till 600Psi.Experimental data were verified using several adsorption isotherms such as Langmuir, BET, Dubinin-Astakhov (D-A) and Dubinin-Radushkevich (D-R). The Langmuir isotherm model was failed to predict the data accurately. The D-A model gave an enough satisfactory representation suggesting that the pore filling model proposed by the Polany. Sorption studies conducted at 30, 31.1, 40 and 50°C revealed that adsorption decreased with increase in temperature. These values were also compared with those obtained through the characteristic plots defined by the Dubinin-Ashtakov equation. CO_2 adsorption behavior at new temperature fit in with the experimental data reported for CO_2 adsorption below its critical temperature. The effect of particle size was studied by considering samples of 150µm, 650µm and 850µm and it was found that adsorption capacity decreased with increase in particle size. As far as the effect of pH was concerned, the adsorption capacity was highest for acidic media followed by alkaline media and neutral media.

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NOMENCLATURE:

V	Sorbed volume
V_L	Langmuir volume
b	Pressure constant
P	Pressure
P_L	Langmuir pressure
P_o	Saturation vapor pressure
V_m	Monolayer volume
C	Empirical constant
n	Number of layers in BET equation/ D-A equation exponent
A	Adsorption potential
R	Universal gas constant
T	Absolute temperature
D	Empirical constant
n	D-A equation exponent
V_v	Void volume

Z	Compressibility factor
ρ	Density
V_o	Micropore volume

Chapter 1

Introduction

Introduction

1.1. Global warming and CO_2 level in atmosphere

Economic growth, energy use and greenhouse gas (GHG) emissions have reflective linkages in developing countries (IPCC 2000). Growing industrialization, increasing incomes, rapidly rising transport and modernizing agriculture have led to rapidly rising energy consumption in India over the past decade. The Indian gross domestic product (GDP) has grown at 5.7 percent per annum during the eighties and above 6 percent during the nineties (GOI 2000). Indian energy use has grown faster than GDP for the last twenty years now (GOI 2000; CMIE 1999). Carbon emissions have almost grown parallel to energy use (Amit Garg et al., 2003). These carbon emissions are primarily responsible for global warming. One of the most universal and vital issues faced by government and industries is global warming and the related climate change. Significant dispute on what are the right strategies is still continuing so as to implement on reduction in emissions of carbon dioxide (CO_2) and other gases such as methane (CH_4) and nitrous oxide (N_2O) to the atmosphere. These gases, also known as greenhouse gases (GHG), have been related to the earth's temperature, term global warming resulting global climate change (W. D. Gunter et al., 1998). Though there has been continuous increase in green house gases, yet world aims for the decrease in green house gas emission (D.R.Vite et al., 2004). Among the various gases responsible for global warming, CO_2 is the major contributor causing 60% of present number of effects (Ykihiro et al., 2003). The primary source of atmospheric CO_2 emissions is the burning of fossil fuels that leads to increase of the CO_2 concentration in the atmosphere (P. Dutta et al., 2008).

1.2. Methods to reduce CO_2 level in atmosphere

Recent concern about increasing concentrations of CO_2 in the atmosphere has encouraged researchers to investigate various methods in order to reduce the emission of CO_2 from point source such as coal-field power plants, natural-gas burning source etc(Y.B. Melnichenko et al., 2009). Significant steps have been taken to reduce the release of CO_2 to atmosphere. However the already present CO_2 in the atmosphere is challenging. Among all the techniques carbon dioxide sequestration is the promising method for reducing the CO_2 from the atmosphere. Sequestration technique involves the adsorption mechanism to reduce the CO_2 from the

atmosphere. One way of doing this is to permanently store away the CO_2 by capturing from the atmosphere. The underground locations are the best possible sinks. However, it is much difficult to store CO_2 on somewhere on the surface. Apart from that for reducing the CO_2 level in the atmosphere the process of adsorption of CO_2 on the surface of some solid capable of acting as a physical adsorbent will be a better solution. A lot of physical adsorbents available for adsorption of CO_2 like, sandstones, sedimentary rocks in dry oil fields, deserted coalmines, off-shore outdated oil fields and deep seated coal seam are available. In this work we have concentrated upon the testing of adsorption of CO_2 on the deep Indian coal seams because coal has been found to be a potential CO_2 sink.

1.3. Coal as a geological sink

India has abundant coal sinks, many of which are barren after reaching the Unminable depth. Coal is the abundant domestic energy reserve in India (Amit Garg et al., 2009). India emitted 1751 million ton (Mt) CO_2 equivalent greenhouse gases in 2005(Grag et al., 2006). Sequestering the CO_2 gas on coal is the example of geological sequestration. And it has also been recognized as an environmentally attractive method to reduce the greenhouse gases emission. Coal which is formed through the physical and chemical modification of peat, by process involves bacterial decay, compaction, heat and time, is an agglomeration of many different complex hydrocarbon compounds. Coal can be divided in four major ranks, anthracite coal, bituminous coal, sub-bituminous coal, and lignite coal (Francis W. et al., 1961). The basic idea of Sequestering CO_2 in to coals is to displace the methane from the coal and to permanently store the CO_2 in coal. Injecting CO_2 in deep coal is still in primary stage. For implementation of this technique, it is essential to understand the mechanism of binary adsorption of methane and carbon dioxide on coal, better sorption property of coal, and ability of carbon to displace methane from coal. Understanding the chemical interaction between methane, carbon dioxide and coal in an aggressive environment is essential. There have been some laboratory experiments to study the enhanced methane recovery, and a few pilot-scale projects to study the adsorption of CO_2 and methane and mixtures at different composition, temperature and pressure conditions to understand the sorption mechanism.

1.4. Factors affecting CO_2 adsorption on coal

The amount of CO_2 adsorbed on the coal depends on the number of factors. The nature of the coal will determine the maximum adsorption capacity under a given set of conditions. The amount of CO_2 adsorbed on the coal will depend on the physical and chemical reactions between coal and CO_2. Parameters such as temperature, pressure, particle size and pH are expected to have reasonable to huge influence on the adsorption of CO_2 on the coal. And we have studied these effects on the sorption of CO_2 on coal. The sorption of CO_2 on coal depends on another two important parameters such as porosity and surface area. Initially if the coal is dry, coal seams become wet as a result of drilling operations, fracturing of the coal bed and over lying layer and the deposition of a combustion gas which contain residual water of combustion. In natural systems pH is an important parameter and will change during sequestration (K.Schrooder et al., 2004). It is well recognized that adsorption of CO_2 on solid surfaces is effected by the pH of the surrounding media (K.Schrooder et al., 2004). The amount to which pH change will affect the CO_2 adsorption capacity of coals has not been investigated in detail (Speight et al., 1994). Coal contains a wide variety of organic and mineral phases in a complex, porous, three-dimensional network which varies from one coal deposit to another from one location to another within the same seam. The organic part of the coal is believed to capture CO_2 using surface adsorption, pore filling and solid solution. The nature of the coal seam itself is a very important variable to be considered. This is why the elemental chemical elements of the coal is important. India has a long history of commercial coal mining covering nearly 220 years starting from 1774 by M/s Sumner and Heatly of east India Company in Raniganj coalfield along the western bank of river Damodar. India now ranks 3rd amongst the coal producing countries in the world. According to the 2008 BP statistical energy survey, India had end 2007 coal reserves of 56498 Million tones, 6.66% of the world total. India being one of the developing countries produces lots of CO_2 from the burning fossil fuels. At the same time the country is also rich in deep coal reserves. The study of adsorption of CO_2 was carried out with samples obtained through Essar Explorations and Production India Limited (EEPIL) from the Raniganj formation in West Bengal. Awareness of extent to which coal can adsorb CO_2 under a variety conditions is necessary to estimate the long-term storage capacity of candidate seams. The nature of the coal will determine its adsorption capacity, but the dynamic nature of the sequestration environment will determine the amount to which that capacity can be understood. In order to estimate the long-term storage capacity of coal

seam, possible changes in the sequestration environment need to be explored and their effect understood.

1.5. Objective of the project

- The primary objective of the present work is to understand the sorption behavior of coal in presence of pure CO_2 gas.
- The second objective is to fit the sorption data of the resulting gas to various isotherm models.
- To study the influence of various parameters such as Particle size, pH, temperature of coal seam on gas adsorption behavior.
- Finally to use characteristic curve concept to CO_2 adsorption data so as to predict the isotherm at new temperatures of the coal seam.
- The predicted values are compared to the experimental values.

Chapter 2

Literature Review

Literature Review

Generation of CO_2 from fossil fuel combustion is a significant contributor to greenhouse gas emission and thereby leads to increase in global warming. Sequestering CO_2 in geological reservoirs is an environmentally attractive option to mitigate greenhouse gas emission. Among the various geological reservoirs, deep coal beds have a great potential. India has vast coal reserves, of which many are un minable after reaching the coal depth 1000 ft. Hence deep coal seams are an attractive option to store CO_2 gas. It is the most promising option because it has an added advantage to recover the methane gas which is entrapped inside the coal. Another advantage is that, after being injected into the coal bed, there is little risk of sequestered CO_2 leaking back to the overlying strata or the atmosphere since it is believed that the pressure maintained by the in situ water would prevent the injected gas from coming out of the coal.

2.1. Comparison of sorption characteristics on different coals

Geological properties of coal seams play a key role while selecting such sinks. Several researchers studied the effect of adsorption of CO_2 on the different coal samples. S. Mazumder et al., 2006, conducted experiments in the laboratory scale with the Silesia coal samples. They conducted the adsorption tests with pure CO_2 and flue gas. Adsorption isotherms of CO_2 and flue gas were measured up to 11Mpa using volumetric method. Their results shows that the excess sorption capacities for CO_2 for wet Silesia coal samples ranged between 1.9 and 1.3 mmol/g respectively. Flue gas sorption capacities on dry and wet Silesia coal samples ranged between 0.45 and 0.2 mmol/g respectively, at pressure of 8Mpa. Their experiments indicate that CO_2 is by far the favored sorbing component for both wet and dry conditions. They also observed that the adsorption of CO_2 onto coal is not significantly slowed down by the addition of other gases, other than dilution effect of pressure.

Fulton et al., 1980, conducted experiments with dry and saturated coal cores of 3 $^1/_2$ inches in diameter. The coal core was saturated with methane to certain degree of saturation. The adsorbed methane was then produced by desorption by the process of reduction of the pressure, i.e., venting out to atmosphere. After natural desorption s stopped producing methane, CO_2 was injected in a repeated trend i.e., CO_2 injected followed by a short period of CO_2 adsorption and methane production. The injected CO_2 was able to completely remove the adsorbed methane.

Ronny pini et al, 2009, conducted the adsorption isotherm experiments on the Australian coal samples. The pure gas experiments were carried out using a magnetic suspension balance, where as in the multi component this technique was coupled to gas-chromatography to obtain the exact fluid phase composition. Single component adsorption isotherm of CO_2, CH_4 and N_2 at 55^0C on the Australian coal samples have been measured by two different laboratories using two gravimetric techniques. High pressure pure adsorption isotherm have been obtained at 45^0C and 60^0C up to 200 bar for two coal samples from Italy and Japan, respectively. Their results shows the usual behavior of excess adsorption isotherms and the two samples show different similarities to CO_2, with the maximum of the excess adsorption and sorption isotherms per unit mass dry coal ranging between 6% and 10%.

Ekrem Ozdemir et al., 2004, conducted the adsorption and desorption isotherms of CO_2 on dried Argonne premium coals samples. Hysteresis was detected between adsorption and desorption. The hysteresis was small or negligible for high rank coals but observable change in behavior of hysteresis was observed for low rank coals. The isotherms were characterized by straight lines and to fit a predictable adsorption isotherm poorly. The characterization by straight line shaped isotherm was related to the solubility of the CO_2 in the coal and to coal swelling.

Wang Zuo-tang et al., 2009, studied the adsorption and desorption of carbon dioxide, methane and other gases on Zhonglisngshan coals experimentally. Their studies show that adsorption is one on of the major concern for both CO_2 sequestration and methane recovery process. The experiments were carried out using both single and multi-gas component mixtures at 25^0C and 30^0C with the highest pressure of 12Mpa, the coal was under moisture equilibrated conditions. Their results show that adsorption capacity of pure CH_4 was higher than the pure N_2 adsorption capacity but lesser than the CO_2 adsorption capacity. The injection of CO_2 in to the coal considerably affects the CH_4 desorption. This allows the CH_4 recovery from the coals, thus supplying more clean energy while sequestrating CO_2 in to the coal seams thereby reducing the greenhouse gas effect.

Razinik et al., 1984, carried out a set of experiments and injected CO_2 at different pressures into large cores to methane and water saturated bituminous coal, and additional simulation study was conducted to calculate the increase in improvement of methane. CO_2 injection increased the recovery of methane by factor of two to three times that achieved by pressure draw down.

2.2. Effect of temperature on CO_2 adsorption

A. S. Azmi et al., 2006, conducted the adsorption studies on the Malaysian coal samples. Their studies involved carbon dioxide adsorption profiles of coal samples of varying mean size distributions ranging from1000µm to 2000µm. They observed that the coal samples having smaller mean particle size distribution of 1000µm show a better rate of adsorption compared to the 2000µm size distribution. These Malaysian coal samples were studied for CO_2 adsorption at varying temperatures (24.6^{0}C, 30^{0}C, 40^{0}C and 50^{0}C). The adsorption capacity of the coal sample shows a inverse response to temperature change.

K.Schroodre et al., 2004 conducted the adsorption test on Argonne premium coal samples using a manometric technique. They studied the sorption characteristics at different temperatures (22^{0}C, 30^{0}C, 40^{0}C, 50^{0}C). They observed that adsorption capacity of coal samples shows an inverse response with temperature. This is attributed to decrease in the adsorption equilibrium capacity with increasing temperature because higher temperatures increasingly favor the gas phase due to T*S entropy term in the free energy expression. Every et al., 1972, conducted experiments to find the ability of carbon dioxide, helium and air to displace methane from crushed coal. Their data showed that carbon dioxide was able to displace 90 percent methane under laboratory conditions. CO_2 was three times more effective than air, and five times more effective than helium in displacing methane from coal.

2.3. Desorption studies

Andreas Busch et al., 2003, studied the methane and CO_2 sorption and desorption measurements on dry Argonne premium coal sample with pure gas components and mixtures. The sorption experiments were performed on powder form on (-100 mesh), dry coal samples. CO_2 sorption measurements were carried out at 22^{0}C up to final pressure of 51 bars, but methane sorption experiments were carried out at same temperatures as for CO_2 sorption experiments but the final pressure was up to 110 bars. The coal samples cover a maturity range from 0.25% to 1.68% vitrinite reflectance. The maceral compositions were dominated by vitrinite reflectance ranging from 85% to 91%. Inertinite contents ranged between 8% to 11% and liptinite contents are 1%. The final ratios of pure CO_2 and methane in molar units on the five coal samples varied between 1.15 and 3.56. The north Dakota Beluah –Zap samples contain vitirnite reflectance 0.25% has the

lowest sorption capacity of 1.15. The low-rank coal sample containing the vitrinite reflectance in range 0.32% and 0.48% attained a highest ratio of sorption capacities of 2.7 and 3.16, while the ratio decreased to 1.6-1.7 for high rank coals. The CO_2/CH_4 mixture gas adsorption tests were conducted to study the degree of preferential sorption of these two gases on coals of different rank. These experiments were conducted on dry coal samples at 45^0C and pressure up to 180 bars. For the highest rank coals the superior sorption behavior of CO_2 and superior desorption of CH_4 were observed. For the low rank coals the preferential adsorption of CO_2 observed in the low pressure region, but the preferential desorption of CH_4 was observed over the entire pressure range.

Puri et al., 1990, carried out a laboratory a simulation study of nitrogen injection, and observed that the recovery and rate of recovery of methane can be increased by stripping the methane off coal by N_2 flooding. Chaback et al., 1996, observed the simulation study of ECBM with pure CO_2, N_2 and their mixtures. In all three cases, it was observed that the increasing methane production was improved by more than a factor of two, and the bulk of the methane was produced much earlier compared to the primary method. Wolf et al., 1999, conducted laboratory and simulation to study the improvement of methane production by injecting the carbon dioxide in the Belgian and German coals. They injected the CO_2 in different rates. Both the experiments show the results that better methane production and carbon dioxide storage. Some field investigations for ECBM recovery and carbon sequestration have already started. In 1995, meridian started a CO_2 pilot plant test in the San Juan Basin in Mexico. A micro – pilot field test for ECBM and CO_2 injection is currently being carried out in Alberta (Canada) by Alberta research council (Gunter et al., 1997.)

2.4. Binary mixtures of gas sorption behavior on different coals

Many researchers have conducted sorption experiments and analyzed the sorption of different coals on binary mixture of gases. Ruppel et al., 1972, studied the adsorption of methane and ethane on dry Pennsylvanian coals to a pressure of 40 atmospheres and at temperatures of 20^oC, 30 ^{o}C and 50^0C, and binary adsorption isotherm data using the ideal adsorbed solution theory (IAS) (Myers et al., and Prasuntiz et al., 1965). The IAS theory was able to describe the methane

and ethane binary adsorption on coal practically. (Saunders et al., 1985) used a stagnant system to study the adsorption of H_2-CH_4 mixture on Pittsburgh bituminous coal at temperature varying from 22^0C to 207^0C, and pressure up to 4.1Mpa.the ideal adsorption solution theory failed to predict the pure component isotherms. (Stevenson et al., 1991) studied the adsorption isotherm for binary, ternary mixtures of methane, carbon dioxide and nitrogen on dry Australian coal samples at 30^0C and pressure up to 5.23Mpa. The equilibrium gas phase and adsorbed phase was differing a lot. The IAS theory was able to provide good predictions for binary mixtures adsorption equilibrium. While the Real Adsorbed Solution theory could not do so accurately. (Arri et al., 1992) studied the binary sorption characteristics of methane – nitrogen and methane – carbon dioxide mixtures on Fruitland coal of the San Juan Basin at 46.1^0C and pressures of 3.45, 6.9 and 10.35Mpa.Their results shows that each gas did not sorbed independently. Instead gases were competing for the same sorption sites. For reasonable data correlation they used the Extended Langmuir Model. Harpalani et al., 1993, studied the pure adsorption of methane, carbon dioxide and a three component gas mixtures containing of 93% methane, 5% carbon dioxide, and 2% nitrogen on moist Fruitland coal from the San Juan Basin at 112^0F and up to pressure of 10.35Mpa. The experimental data of mixtures was compared with theoretical prediction by numerical method and Extended Langmuir Model. The theoretical predictions were in good agreement with experimental data for both the models, the Extended Langmuir model was better than the numerical technique. Greaves et al., 1993, studied the sorption characteristics using Sewickley coal samples at 22.7^0C and up to pressure 6.9Mpa. They studied the adsorption of pure methane, carbon dioxide and their mixtures (90%CH_4 + 10% CO_2 and 75% CH_4 and 25% CO_2). Their results show that the sorption capacity of carbon dioxide on coal is much greater than the methane. Considerable sorption hysteresis was also observed during desorption for both gases.

Hall et al., 1992 conducted a significant sorption tests using wet Fruitland coals at 115^0F and pressure up to 1800Psi. They studied the adsorption of nitrogen, methane, carbon dioxide and their binary mixtures. The Ideal Adsorbed Solution Theory and various two-dimensional equations of state (EOS) models described the pure component and mixed-gas adsorption data with reasonable accuracy and were better than the traditional Langmuir model.

Chaback et al., 1996, studied the sorption data for N_2, CH_4, CO_2, and their mixtures on a number of bituminous coal and used those data to examine the reasonable demonstration of sorption behavior for use in reservoir engineering studies including mixtures of two and three components. Busch et al., 2003, conducted adsorption studies with mixtures of methane and carbon dioxide on dry and moisture equilibrated coals of different rank, composition of different European coals. All measurements did not show preferential sorption of carbon dioxide and desorption methane. The sorption behavior varied with pressure range.

2.5. Isotherms

Various isotherms for adsorption of gases on solids have been analyzed using different approaches such as Langmuir theory, BET theory, Polanyi's Potential theory. In addition, there are several semi-empirical approaches to describe the adsorption of gases on solids.

2.5.1. Langmuir isotherm

However, the most commonly used model is Langmuir model that describes Type I isotherm and has been extensively used for adsorption of methane and CO_2 on coal. Langmuir model is based on the assumption that there exists a fixed adsorption sites on the surface of the solid and only one gas molecule is adsorbed at a single adsorption site. Moreover the adsorbent surface is energetically homogeneous and that the energy of adsorption is constant for all sites with no interaction between the adjacent adsorbate molecules.

The equation for the Langmuir isotherm is given as:

$$\frac{V}{V_L} = \frac{P}{P + P_L} \tag{2.1}$$

where, V is the adsorbed volume at equilibrium pressure P, b is the pressure constant, V_L is the Langmuir volume and P_L is known as Langmuir pressure.

This model has been used to describe methane adsorption data on coals over a wide range of temperatures and pressures with a good fit (Yee et al., 1993). As per the Langmuir model it is believed that the surface of the solid should be energetically homogeneous, which is not so in the case of coal. Hence this model has limited application to CO_2 adsorption on coal.

2.5.2. BET isotherm

In 1938, Brunauer et al., modified some of the assumption of Langmuir model and provided an extended Langmuir model for multilayer adsorption popularly known as the Brunauer, Emmet, and Teller (BET) model. This model assumes that the surface of the adsorbent is energetically homogeneous with no interaction between the adsorbed molecules. Moreover, the heat of adsorption is equal to the molar heat of condensation in all layers except for the first layer which acts as a stack. At saturated vapor pressure, the adsorbate condenses to liquid on the surface of the solid leading to infinite layers. The BET isotherm equation is given as:

$$\frac{1}{V(P_o/P-1)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\frac{P}{P_o} \tag{2.2}$$

where, V_m is the monolayer volume, C is a constant, P_o is the saturation vapor pressure, and the remaining variables have their usual meaning. Although BET equation does not entirely fit into the experimental data, yet it is a useful tool that provides a theoretical foundation for the various isotherms shapes (Lowell and Shields, 1984). The validity for the BET model ranges between relative pressure values of 0.05 to 0.35 (Gregg and Sing, 1982).

2.5.3. Polanyi's potential theory of adsorption isotherms

Polanyi's potential theory of adsorption assumes the existence of a potential field around the surface of the solid into which the adsorbed gas molecule falls. The adsorption potential is the work done per mole of adsorbate needed in transferring molecules from the gaseous state to adsorbed state. It implicates the work done by temperature-independent dispersion forces. Therefore the potential curve is independent of temperature, and is typical of the particular gas-solid system alone. It is a function of the enclosed volume surrounding the adsorbent surface. Hence, the adsorbed volume is a function of adsorption potential (A) alone given as:

$$V = f(A) \tag{2.3}$$

The above relation is typical of a gas-solid system, and is called the characteristic curve (Yang, 1987). The characteristic curve generated from one experimental isotherm thus helps to predict the isotherms at different temperatures (Mehta, 1982). Considering the adsorbate behaves as an ideal gas, the adsorption potential is given as:

$$A = RT * \ln\left(\frac{P_o}{P}\right) \tag{2.4}$$

where, R is the Universal Gas Constant, A is the adsorption potential, T is the adsorption temperature in absolute units, P is the adsorption pressure and Po is the saturated vapor pressure of the adsorbate at definite temperature T.

In 1967, Dubinin described adsorption on microporous adsorbents and proposed a new theory known as the theory of volume filling of micropore (TVFM). Coal being a microporous adsorbent as its pore size ranges below 20 nanometer. Thus the mechanism by which adsorption of microporous solid occurs is restricted to volume rather than their surface. Dubinin (1975) thus introduced a new theory called the Theory of Volume Filling of Micropore that postulates that, in micropores, the adsorbate occupies the pore volume by the mechanism of volume filling, and does not form discrete layers in the pores. In 1995, Dubinin and Astakhov proposed an equation based on this theory that represented the isotherms that obeyed the TVFM. The Dubinin-Astakhov (D-A) equation, it is expressed as follows:

$$V = V_o * Exp\left[-D * \left\{\ln\left(\frac{P_o}{P}\right)\right\}^n\right] \tag{2.5}$$

where, V is the amount adsorbed, V_o is the micropore volume, n is the structural heterogeneity parameter that varies between 1 and 4, D=(RT/βE)n is a constant, where, E is the characteristic energy of the adsorption system, T is the absolute temperature, R is the Universal Gas Constant, and β is the adsorbate affinity coefficient. D is a constant for a particular adsorbent-adsorbate system, and is determined experimentally. P_o is the saturation vapor pressure of the adsorbate at temperature T, and P is the equilibrium free gas pressure. Dubinin and Radushkevich restricted n = 2 for some cases, and modified the equation to Dubbin and Radushkevich equation (D-R) as below:

$$V = V_o * Exp\left[-D * \left\{\ln\left(\frac{P_o}{P}\right)\right\}^2\right] \tag{2.6}$$

D-A and D-R equations are both called Polyani equation and can be suitably applied to predict the adsorption behavior of the same soild adsorbate at an unknown temperature with the help of characteristic plot.

Chapter 3

Materials & Methods

Materials& Methods

3.1. Coal samples and preparation

Coal samples from Raniganj East CBM Block through EEPIL belonged to Gondwana coal of Permian age and were received from each bore holes at various depths as illustrated in Table 1. (Hajra et al., 2003).

Table 1: Coal Samples and location:

Sample Number	Drill Hole	Depth (Range in m)
S-1	EDC #	1197.0-1197.3
S-2	EDC #	631.00-631.24
S-3	EDC #	982.06-982.26
S-4	EDC #	864.71-864.98
S-5	EDC #	1079.40-1079.70

The coal samples were crushed, grounded and sieved through 72-BSS mesh openings. These powdered samples were moisture equilibrated in an environmental chamber at the experimental temperature and 96% humidity. The moisture content of the samples was estimated using the standard test method for equilibrium [ASTM D 1424 – 93]. Then the coal samples were evaluated for the proximate analysis using laboratory furnace as per the standard method [ASTM D 3172 – 07a] and ultimate analysis of coal samples were estimated using CHNS Analyzer [Perkin-Elmer], as per the standard methods [ASTM D 3176 – 09].

3.2. Experimentation

The CO_2 sorption experiments were carried out in self fabricated set up which is described below (Fig: 1). the sorption tests were carried out up to maximum pressure of 800psi.

3.3. Procedure

The line diagram of fabricated set up represents reference gas chamber (FV), sample chamber (SC); pressure transducer (PT). The pressure transducer helps to measure the pressure in the sample chamber as well as the reference chambers. A micro filter not visible in figure was placed just above the sample chamber to prevent loss of samples during the application of vacuum. The entire fabricated set up was immersed in a constant temperature water bath to maintain the constant temperature. The amount of adsorbed volume was estimated at a constant temperature as a function of gas pressure at equilibrium. The equilibrium at each isotherm point is achieved at a constant pressure within 6-8 hours. In addition Real gas law was also applied to measure the adsorbed volume. Peng-Robinson Equation of State was used to calculate the compressibility factor in real gas equation. The fixed volume and the void volume were measured using Helium gas expansion. After conducting the experiment at constant temperature, pressurized gas was totally depressurized. The whole setup was maintained at constant temperature and the process was repeated for different coal samples.

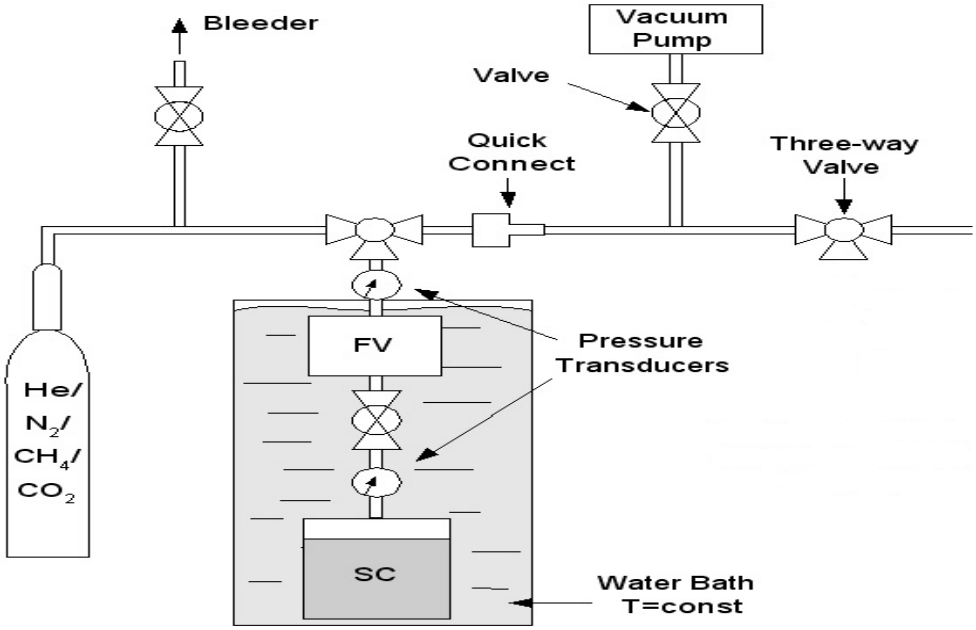

Figure 1: Line diagram of the fabricated setup

It was necessary to estimate the void volume in the sample cell very accurately so as to determine the volume of gas adsorbed with limited error. A minor error in the void volume measurement could lead to significant error in the sorbed gas estimation. In the fabricated setup, the void volume consisted of the adsorbent pore volume, inter-particle voids and the free volume that included up to the valve. Helium gas was used to evaluate the void volume by expanding it from FV to SC and the equilibrium pressure was measured. Helium has the property of not getting adsorbed on coal, hence it was used. To calculate all the volume, ideal gas equation was used. Before charging gas into the unit, it was necessary to evacuate the gas within the sample and the reference cell using a vacuum pump. The equation used to evaluate the void volume is given below:

$$V_v = \frac{\Delta PV_{pVC}}{\Delta P_{SC}} \tag{3.1}$$

Where, Δp denotes the change in pressure due to gas expansion after the valve between the sample cell and the reference cell was opened. Each step was repeated thrice so as to minimize any experimental error.

3.4. Measurement of pure gas

The following procedure was adopted to measure the gas adsorbed in the unit.

Accurately weighed samples were first placed inside the sample cell and were sealed tightly.

Initially, the helium gas used in the void volume measurement was bled out from both the cells. Even then there was some amount of helium present in the cells which was got ridden by applying vacuum. Now the pressure of the sample cell (P_{s1}) and reference cell was recorded through the pressure transducer connected to the data acquisition system and was reflected in the computer screen attached to it.

The sample cell was isolated from the reference cell by closing the valve in between.

Now the CO_2 gas was fed into the reference cell by 150 units, and then the valve connecting to FV was closed. Now the gas was allowed to equilibrate and the pressure reading was recorded as P_{r1}.

The valve between the sample and reference cell was opened, and the gas from the reference cell flows into the sample cell and gets adsorbed in the sample. After equilibrium is attained, the pressure reading for both the sample cell (P_{s2}) and reference cell (P_{r2}) were recorded.

To calculate the moles of gas that adsorbed in the coal samples in the sample cell it was necessary to calculate the number of moles of gas that left FV, and the number of moles of gas that appeared in the SC as free gas in the void volume. Again a mass balance analysis was carried out.

To obtain isotherm at next higher pressure, the valve between the SC and FV was closed. Now the valve connecting the inlet gas and the FV was opened to inject the gas to next 150 units. The valve was closed and the equilibrium reading in the FV was recorded. Same procedure was repeated for the next increment in pressure till isotherm is reached.

Now to obtain the desorption steps, the gas in the FV was first released by 150 unit and the pressure was recorded after equilibrium was attained. Now the valve between the sample cell and the reference cell was opened and the gas was allowed to flow from the sample cell (SC) to the reference cell and the pressure reading was noted till equilibrium was achieved. Same procedure was repeated till the minimum pressure was present in the sample cell and the desorption isotherm is plotted.

3.5. CO_2 sorption calculations

Gas adsorption data were obtained using a volumetric apparatus (Figure-1). The volumetric apparatus immersed in the constant temperature water bath maintained uniform temperature in the adsorption study. The pressure transducers were connected to Data Acquisition System (DAS). The adsorption data were collected through the DAS with compatible software installed on a PC. The adsorbed volume was determined at a constant temperature (30^0C, 40^0C & 50^0C) as a function of pressure at equilibrium. The fixed volume and the void volume were determined through helium expansion. Correction for the gas adsorbed at each isotherm step was accomplished assuming the liquid density of the adsorbate. The sample was depressurized to evacuate overnight and moisture equilibrated at the new temperature to study the effect of temperature, after conducting the experiment at one temperature. The temperature of the water

bath was maintained at the new temperature and the process was repeated for the adsorption study with the sample. The photograph of the experimental set up is illustrated in Fig 2.

Fig 2: Photograph of the fabricated experimental set up (Top View)

Concept of volumetric adsorption is based on the phenomena that adsorption removes the adsorbate gas molecules from the free gas phase, resulting in decrease in free gas pressure within the experimental system (Krooss et al, 2002). The difference in the total amount of gas (n_T) introduced into the void volume of sample cell (SC) and the amount of free gas occupying the void volume (n_f) in the sample cell gives the amount of gas sorbed (n_a) in number of moles.

$$n_a = n_T - n_f \tag{3.2}$$

The total amount of gas introduced into the SC during a particular pressure step is estimated using the equation below:

$$n_T = \left(\frac{V}{RT} \times \left(\frac{P_{S1}}{Z_1} - \frac{P_{S2}}{Z_2} \right) \right)_{FV} \tag{3.3}$$

3.6. Modelling of carbon dioxide adsorption data

Different isotherm equations of Langmuir, BET, D-R and D-A models were correlated to the sorption data for CO_2. Langmuir model equation was used to obtain the Langmuir constants V_L and P_L. These values were utilized to establish Langmuir isotherm. Using the estimated saturated vapor pressure, the rest of the proposed model isotherms were established. The direct estimation of its vapor pressure is practiced for the experimental temperature below critical temperature of CO_2 (31.1^0C). The saturated vapor pressure values obtained was used in BET equation to obtain the monolayer coverage (V_m) and BET constant(C). These constants helped to predict the BET isotherm. Similarly, estimated vapor pressure for individual gases was utilized in D-R equation to obtain the micropore volume (V_o) and the constant (D) that predicted the D-R isotherm. D-A equation comprising three parameter such as micropore volume(V_o), constant (D) and structural heterogeneity (n) were obtained using the measured data and estimated vapor pressure to predict the D-A model isotherm.

3.7. Characteristics Curve

Dubinin-Polanyi model has a unique advantage that utilizes characteristics curve to predict isotherms at any temperature from a given one set of data. Characteristic curve is a plot between adsorbed volume and adsorption potential. Adsorption potential signifies the workdone by a temperature independent dispersion force, hence is independent of temperature (Yang. 1987).Hence by using one set of adsorption data at any particular temperature, it is possible to predict another set of adsorption data at another temperature. Hence with the temperature gradient of the coal seam known, the adsorption behavior of the gas can be experimented at the Insitu coal bed temperature which can be utilized to estimate the actual adsorption capacity of the gas at different depth. This feature can also be used to predict the change of sequestration potential because of a change in temperature with CO_2 injection.

Chapter 4

Results & Discussions

Results & Discussions

4.1. Geochemistry

CO_2 estimation on coal samples were done on dry ash free basis. Characteristics of coal is an important parameter that dictates the sorption potential of coal. The proximate and ultimate analysis results are depicted in Table 2 below.

Table2. Proximate and Ultimate analysis results

Sample No.	**Volatile Matter, %**	**Ash, %**	**Moisture, %**	**Fixed Carbon, %**	**Ultimate Carbon, %**	**Hydrogen %**	**Nitrogen %**	**Sulphur %**
S-1	37.0	12.0	0.6	50.4	89.73	3.097	6.93	0.243
S-2	27.0	37.0	3.2	32.8	88.89	4.605	6.24	1.559
S-3	37.0	22.0	1.0	40.0	90.01	4.485	5.29	0.215
S-5	41.0	9.0	1.0	49.0	88.84	4.79	6.17	0.203

From the results it was observed that the ash contents vary between 9% and 22% except for one sample that showed an irregularly high ash content of 37%. No such irregular behavior was observed either for volatile matter or moisture content. While Indian coals are said to be high ash contents with a mean value of 44% (Garg. A et al., 2009). In this case the coal sample from Raniganj had very low ash and moisture content than normal Gondwana coals (Laxminarayana et al., 1999).This result shows superior quality of coal that belonged to sub-bituminous type. In general it is recognized that the fixed carbon of coal increases with increase in coal depth which is directly proportional to the coal maturity (Laxminarayana et al., 1999), which is true for Indian coals as shown in Table 2.

4.2. Adsorption capacity

The adsorption capacity of CO_2 on coal samples was determined using above described apparatus and procedure described in the previous section. The sorption capacity of coal samples were shown in the Table 3 below. The adsorption capacity of CO_2 on coal samples were measured at the highest injection pressure of CO_2. Sample 1 showed highest potential for CO_2 adsorption.

Table3. CO_2 Sorption capacity of Raniganj coals

Sample No	**CO_2 partial pressure adsorbed(Psi)**	**CO_2 adsorbed (mL/g)**
S-1	875.761	11.86
S-2	652.668	5.15
S-3	806.243	8.35
S-5	657.698	10.09

4.3. Effect of coal depth on adsorption capacity

Coal rank is said to increase with increase in coal maturity and coal depth. It has been supported by the (Lakshminarayan et al., 1999). It is true for coal samples studied as depicted in Table 2. It was observed that the volatile content in coal samples 2 and 3 increased with coal depth, where as this relation was not supported for the sample 1 and 5. One of the reasons could be that the presence of natural heterogeneity of the coal could vary from one bore hole to bore hole as samples 1 and 5 come from different bore holes along the same seam. It indicates there is no definite relationship between the adsorption capacity and volatile matter content. While the adsorption capacity of coal sample shows increasing trend with increasing in coal depth. Hence the adsorption capacity increases with increasing coal maturity. In additional adsorption capacity increases with increase in fixed carbon as shown in Table 2.

4.4. Adsorption of CO_2 on Coal samples

The study of CO_2 adsorption on four coal samples obtained from Raniganj coal seams were studied. The CO_2 sorption behaviors on four coal samples are shown in fig 3.

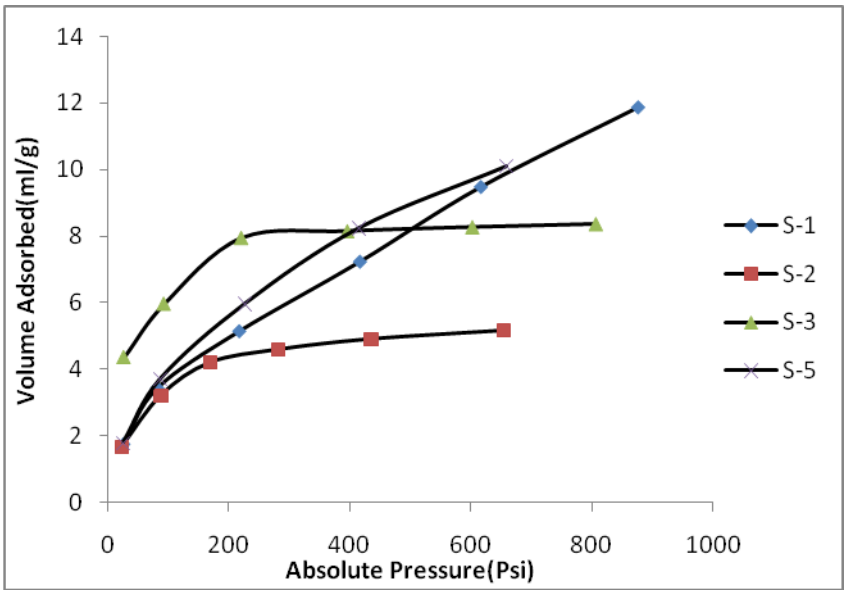

Fig3. CO_2 sorption characteristics on different coal samples

It was observed from fig 3 that the sample 1 displayed the highest sorption capacity 11.86ml/g followed by sample 5 that showed 10.09ml/g. Least sorption capacity was obtained for sample 2. At lower pressure< 200psi adsorption equilibrium was obtained for samples 2 and 3. However sample 3 showed a higher adsorption potential for CO_2. Sample 1 and sample 5 failed to achieve equilibrium even beyond 800 psi. Both these samples showed identical rate of CO_2 adsorption.

S-1 exhibited highest sorption due to the maceral composition of coal. Indian coals have were vertninite, ranging between 22-35%. It is the intrinsic property of virtinite to have low inert materials so as to increase its porosity. Hence higher sorption is attributed due to virtininte composition of coal in S-1.

4.5. Desorption studies

After completion of adsorption of CO_2 on coal sample the samples were tested for desorption studies the comparison of the adsorption and desorption capacities were given in Table 4. Ideally sorption of CO_2 on coal is a physical adsorption process. Being reversible by nature, the

hysteresis should be negligible (Goodman, 2005; Krooss *et al.*, 2002). Table 4 shows the desorption capacity of coal at minimum pressure. It could be clearly visible that the rate of desorption was faster in sample 1. All the coal samples contained gas in the range 1ml/g to 4 ml/g. Hysteresis was minimum in sample 1. Sample 3 and sample 5 showed maximum positive hysterisis. The hysterisis increased with increasing pressure initially and extended till 600 psi and thereafter is reduced (Fig 4-7). However, hysterisis has been reported for CO_2 sorption on coals (Ozdemir et al., 2004). Busch et al. (2003) explained that these hysterisis may be attributed to a metastable sorbent/sorbate system that prevented releases of gas with decreasing pressure during desorption.

Table4. CO_2 Desorption capacity of Raniganj coals

Sample no	**CO_2 partial pressure desorbed(Psi)**	**CO_2 desorbed ml/g**
S-1	80.774	2.5239863
S-2	22.3691	1.29
S-3	23.115	4.16
S-5	24.865	2.21

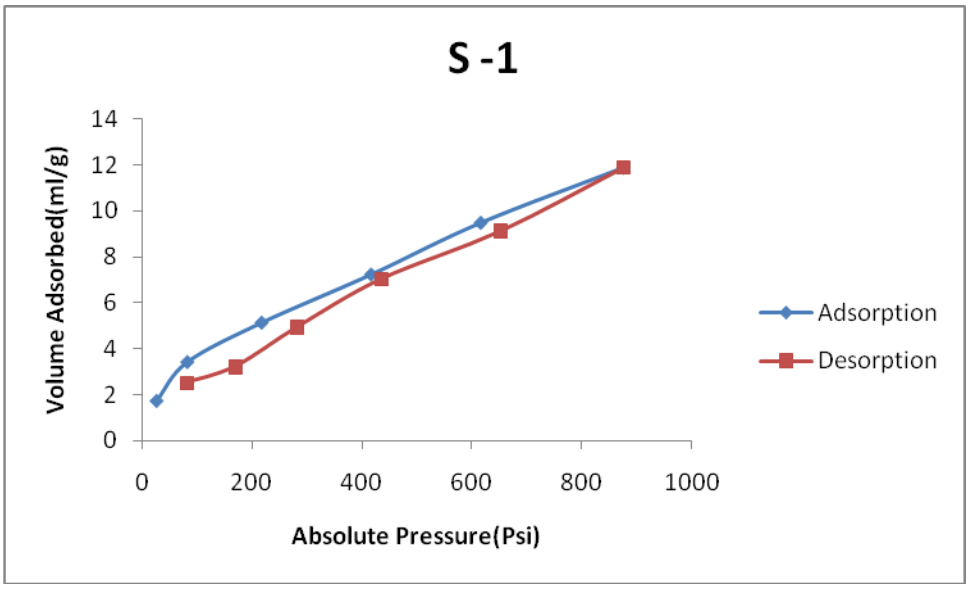

Fig4. Adsorption hystriess for coal S- 1

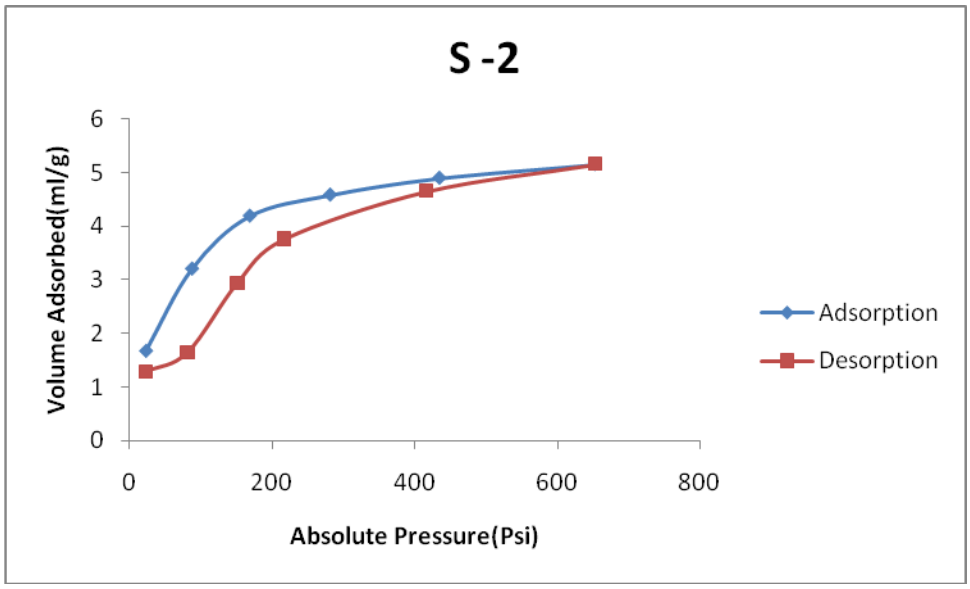

Fig5. Adsorption hystriess for coal S- 2

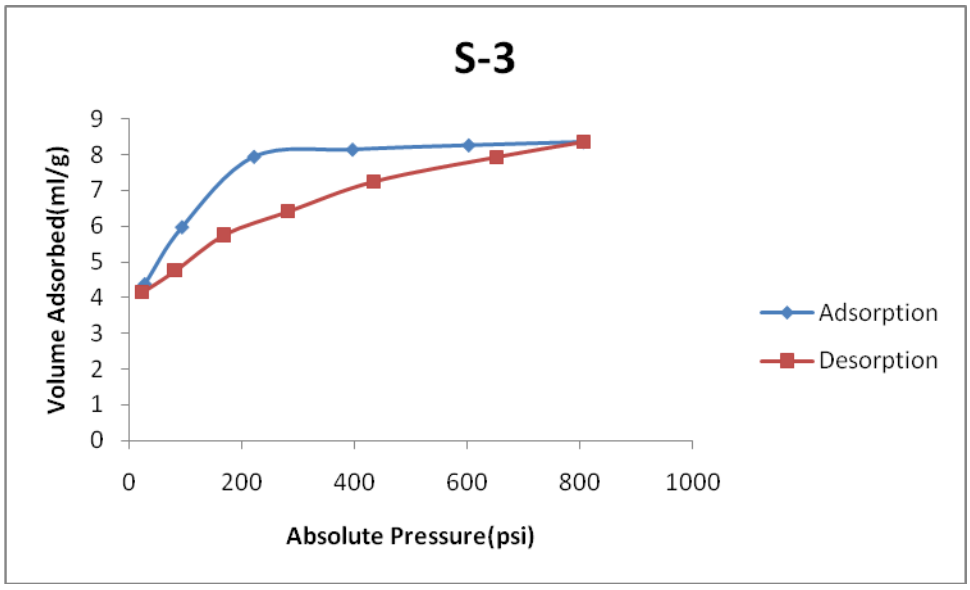

Fig6. Adsorption hystriess for coal S- 3

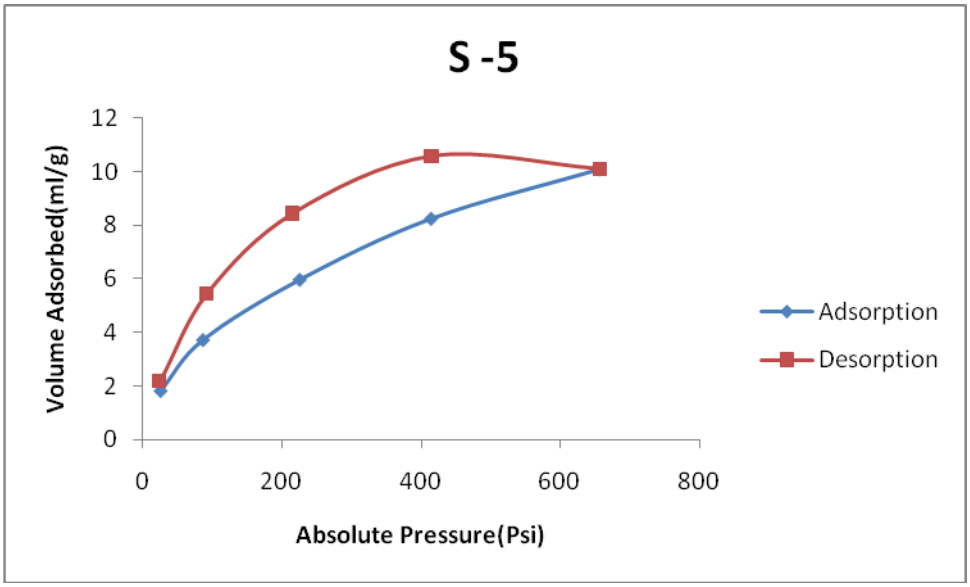

Fig7. Adsorption hystriess for coal S- 5

4.6. Adsorption isotherm models

Various isotherms for adsorption of gases on solids have been analyzed using different approaches such as Langmuir theory, BET theory, Polanyi's Potential theory. The experimental data was used to model the adsorption kinetics using Langmuir model using equation 2. The Langmuir parameters were calculated using linear regression analysis of the experimental data by using SPSS 13.0. The Langmuir parameters data has been given below (Table 5). The comparison between experimental values and parametric Langmuir models has been shown in Fig (8-11). The D-R and D-A parameters were estimated using linear regression analysis and non-linear regression analysis respectively using SPSS 13.0 using eqation (5,6) is represented in Table 5. Comparisions of experimental data to all the isotherm models such as Langmuir, BET, D-R and D-A with respect to each samples are shown in Fig (8-11).

Table5. Parametric values of Langmuir, BET, D-R and D-A isotherms

Sample no	**CO_2 adsorbed, ml/g**	**Langmuir parameters**		**BET parameters**		**D-R parameters**		**D-A parameters**		
		K	V_m	C	V_m	D	V_0	n	D	V_0
S-1	11.86	0.0033	14.71	4.632	11.364	0.124	8.980	1	1.143	12.979
S-2	5.15	0.0168	5.59	18.900	5.291	0.078	5.280	2.125	0.066	5.206

S-3	8.35	0.0338	8.70	39.333	8.475	0.050	8.482	2.102	0.044	8.461
S-5	10.09	0.0048	12.82	6.267	10.638	0.121	8.989	1.143	0.422	12.160

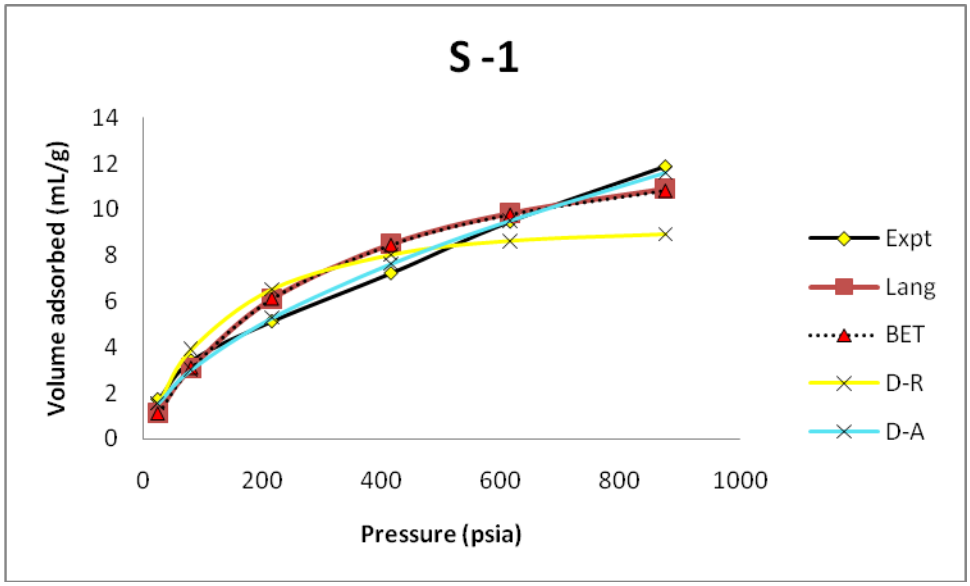

Fig8. Comparison of experimental values with theoretical models for S- 1

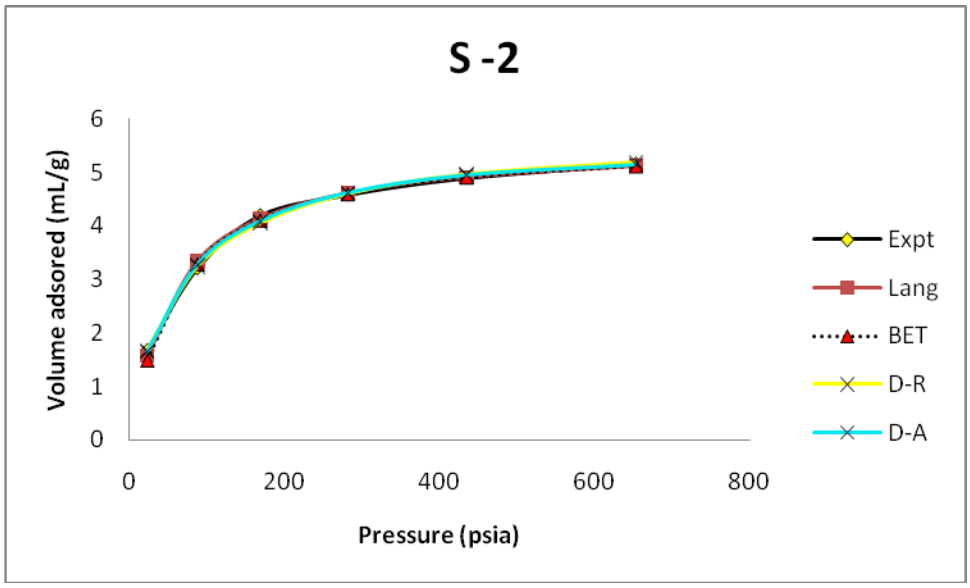

Fig9. Comparison of experimental values with theoretical isotherms for S- 2

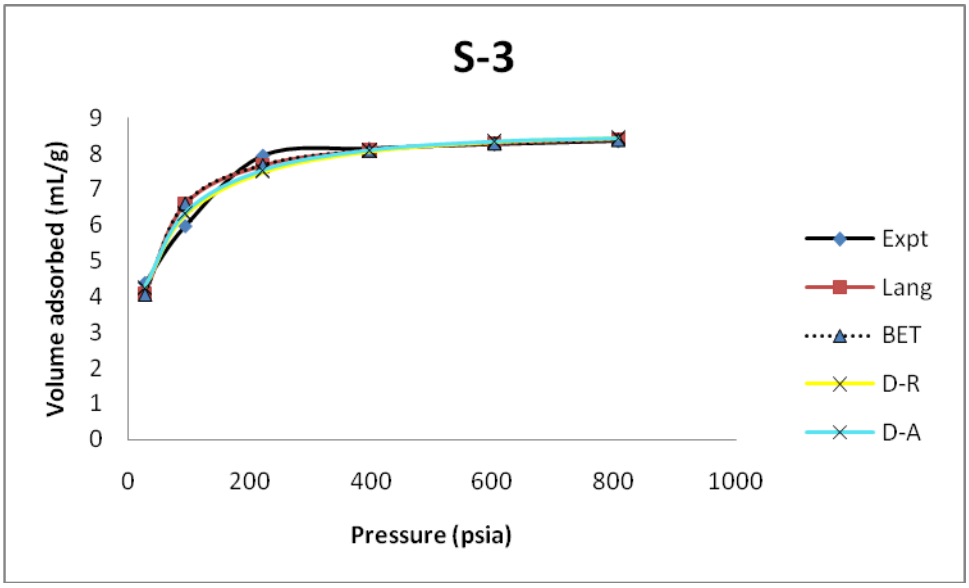

Fig10. Comparison of experimental values with theoretical isotherms for S- 3

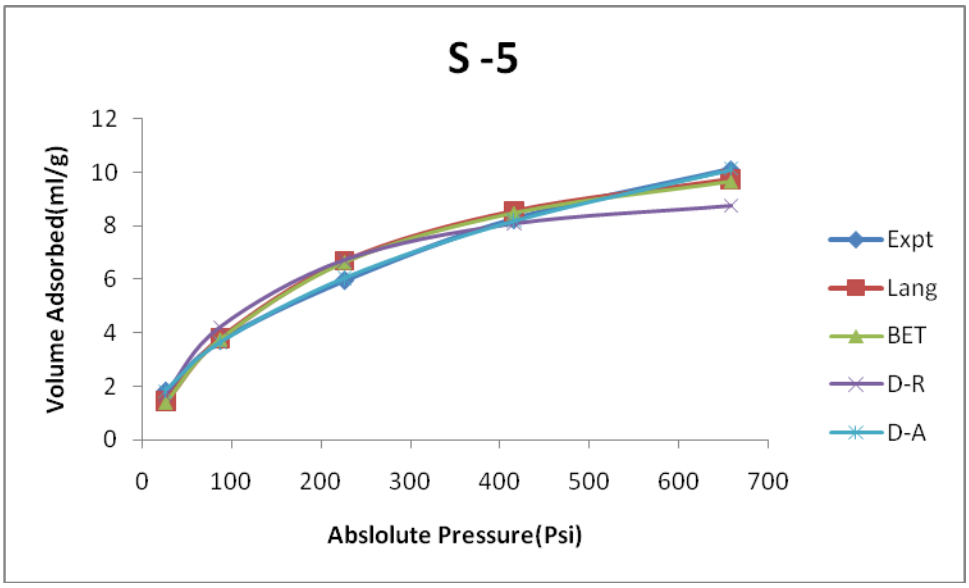

Fig11. Comparison of experimental values with theoretical isotherms for S- 5

From the plots it was observed that Langmuir model satisfies the experimental results to some extent. More deviations exists for sample 1 and 5 at higher pressure which has higher sorption capacities than the sample 2 and 3. For both the samples 1 and 5 Langmuir model fails to predict the sorption capacities at higher capacities and gives a low sorption values. Because langmuir and

BET models account only for monomolecular layer adsorption on the surface, the resultant adsorbed volume given by these models is much lesser. The BET model parameters were given in Table 5 also exhibit similar trend as langmuir isotherm (Fig 8-11). This can be explained by the fact that the BET model has been considered from the simplified equation (2) for multi layer adsorption.

From the figure (8-11) it was observed that the D-R equation fitted well for sample 2 and 3, and it showed much deviation at higher pressure for sample 1 and 5. These results suggests that the parameter n=2 in Polayni's potential theory is not suitable for presntly availble experimental data. The D-A parameters which were calculated using limting constaint $1 \leq n \leq 4$, suggests that n varies between 1 and 1.5 for sample 1 nad 5, while 2 for sample 3 amd 2. The limitations of D-A model even under higher pressure can be seen from the plots of equilibrium pressure against the volume adsorbed at the equilibrium pressure. In addition, D-A has ability of representing all samples perfectly, including those for which Langmuir was a better fit. This appreciates to the fact that the potential theory proposed by (Polanyi, M et al., 1932) has the ability to explain monolayer adsorption in terms of adsorption in micropores through TVFM. A comparison between the D-R and D-A parameters reveal that for S-2 and S-3 as *n* in D-A is closer to 2, the values of *D* and V_o for both D-R and D-A are approximately closer to each other. This is in agreement with the basis with which D-A isotherm was originated.

4.7. Absolute Residual Error

The percentage of Absolute Residual Error (ARE) was used to calculate the percentage deviation of the experimental results from the theoretical models discussed above. The percentage error was calculated using the following equation.

$$\%ARE = \frac{\sum_{i=1}^{j} abs(r_i)}{j} X100 \qquad (4.1)$$

Where r_i is the residual error calculated with the experimental value as the basis and j is the number of data points available for every sample. The percentage ARE values are shown in Table 6. From the ARE results it can be observed that the Langmuir model has highest residual error and D-A has lowest possible error. This justifies the fact that has been presented above as graphical comparison between experimental data and theoretical models. From the Table 6, the %ARE values for Langmuir and BET are found to be comparatively very close. Although D-R accounts for the filling of pores in coal the temperature invariant

parameter n being constant prevents it from representing the experimental results perfectly at high pressures. For sample 2 and 3 %ARE values of both D-R and D-A models are relatively close to each other. Morover the values of D-A suggests that the D-A equation is capable to represent more perfectly the data obtained for sample 1 and 5 for n value is closer to 1. For sample 2 and n values are 2. Maximum 5.30% and 1.17% error obtained for sample 1 and 5 respectively using D-A equation. Langmuir approximation data for sample 2 and 3 are more accurate with a maximum error of 4%. TVFM based D-R and D-A represents data with maximum error not more than 3%.

Table6. Percentage absolute residual errors (%ARE) for Langmuir, BET, D-R and D-A models

Sample	**%ARE-Langmuir**	**%ARE-BET**	**%ARE-D-R**	**%ARE-D-A**
S-1	15.68	15.91	16.20	5.30
S-2	2.26	2.79	1.09	1.35
S-3	3.56	3.71	2.69	2.75
S-5	8.45	8.66	9.57	1.17

4.8. Absolute and Gibbs' values

Gibb'sadsorption theory is defined as a excess quantity representing the difference between the quantity of the adsorptive in a real system and in a theoritical system characterized by the same macroscopic parameters of state as the real systems, but, in which the coexisting phases are homogeneous all the way up to a certain mathematical interface(Serpinskii, V et al., 1985). Most of the studies till date have been conducted based on the Gibbs values of adsorbed gas volume. Thus so far our analysis did not account for gas density changes with corresponding pressure and temperature because it was controlling the adsorption of gas on solid coal. Considering density change Gibb's value will change into absolute values that exhibit greater values corresponding to Gibb's value at higher pressure. The relation between Gibb's and absolute number of moles adsorbed is given as shown by the equation below

$$n_{abs} = \frac{n_{Gibbs}}{[1 - \frac{\rho_{gas}}{\rho_{sorbed}}]} \quad (4.2)$$

Here, gas density in the adsorbed state is assumed to be constant with change in equilibrium pressure and is represented as $\rho_{sorbed} = 1.18 g/mL$. The value of ρ_{gas} is specific to the temperature and pressure at which the gas is adsorbed and also takes into account the compressibility factor to account for non-ideal behaviour of the gas at higher pressures. The comparision of Gibb's and absolute vales are shown in figure (9-12). This value was calculated using Peng-Robinson EOS since the procedure for calculation of volume of adsorbed gas involves the use of the Gibbs theory of the excess gas adsorbed. The values consequently calculated correspond to the value of excess Gibbs' moles adsorbed given by n_{Gibbs}.The comparison between the volume calculated from the Gibbs and absolute values is shown fig (12-15). *%ARE* was calculated for Gibb's and absolue values and is shown in Table 9. As illustrated in the Table 9 , it can been observed that the %ARE increased in all the cases.

Table7. %ARE values for Absolute Langmuir, BET, D-R and D-A isotherm models

Sample	%ARE-Langmuir	%ARE-BET	%ARE-D-R	%ARE-D-A
S-1	17.15	17.36	18.21	7.90
S-2	3.31	3.76	1.57	1.28
S-3	5.00	5.47	2.96	2.54
S-5	9.25	9.85	10.62	1.39

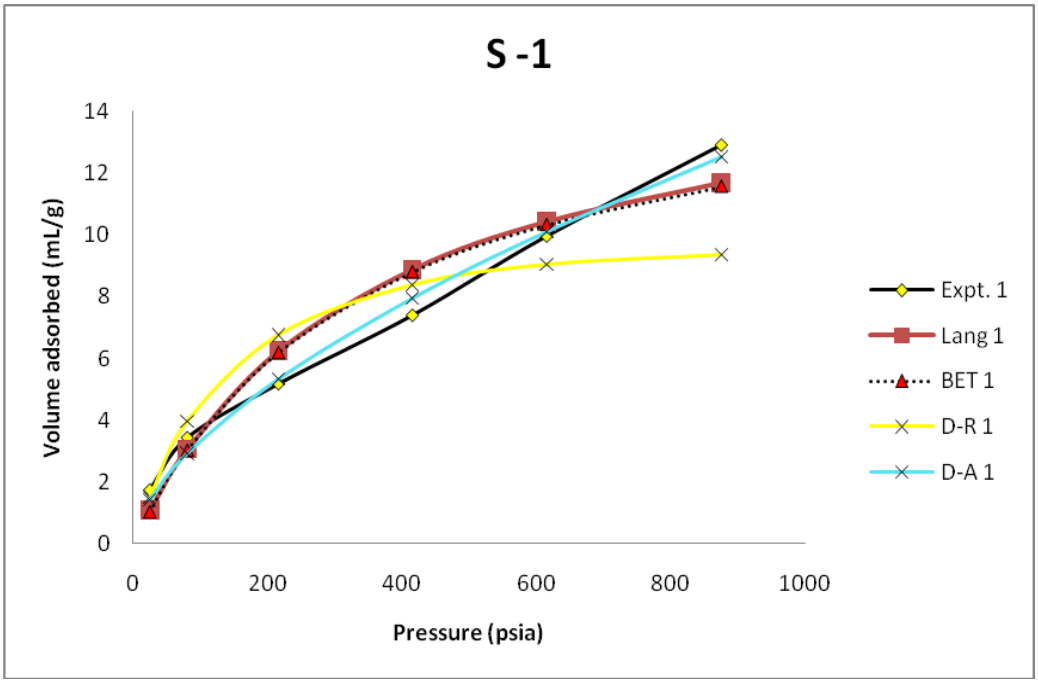

Fig12. Experimental absolute values with theoretical isotherm values for S- 1

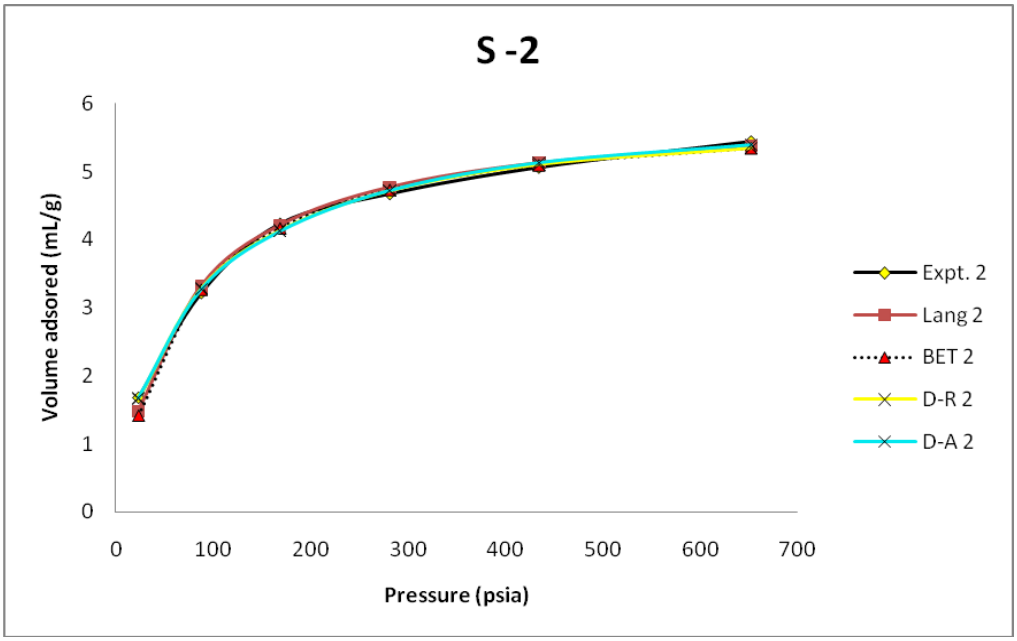

Fig13. Experimental absolute values with theoretical isotherm values for S- 2

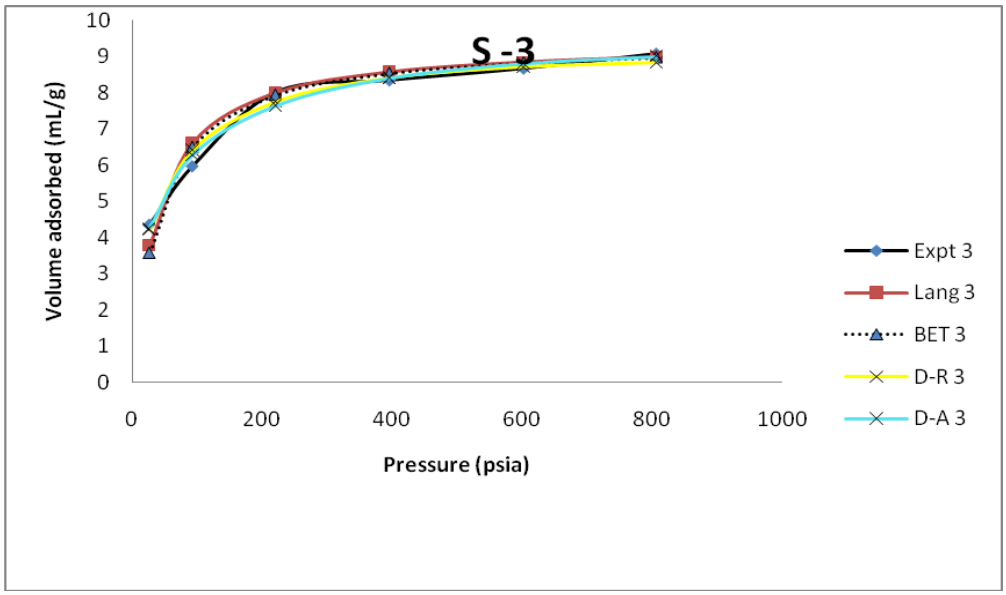

Fig14. Experimental absolute values with theoretical isotherm values for S- 3

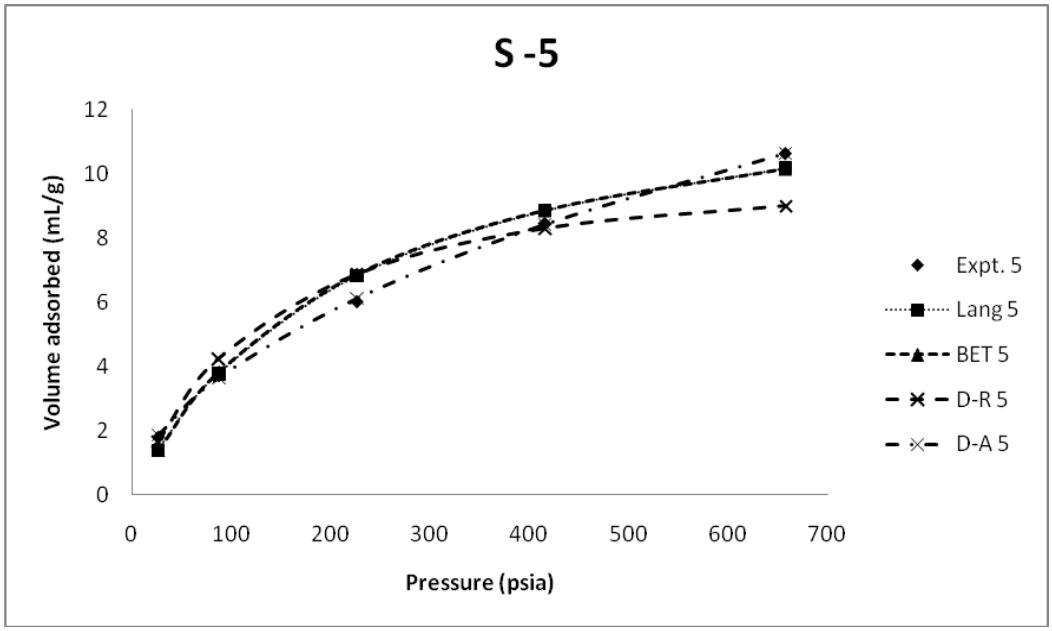

Fig15. Experimental absolute values with theoretical isotherm values for S- 5

4.9. Effect of particle size

Several researchers have studied the effect of particle size on sorption. (Andreas Busch et al, and Yves Gensterblum et al., 2006) were conducted the laboratory experiments on Silesia 315 LW 155 sample of German coals. They had considered the coals of different particle size in the range of (707µm -2000µm and 354µm -707µm) sample show very similar preferential sorption behavior. Another size in medium range 354µm -707µm sample shows a comparable trend to the largest fractions but it shifted to stronger preferential sorption of CO_2. Another size in lower range (63-177µm and <63µm) shows a very strong preferential adsorption of CO_2. The degree of CO_2 sorption clearly increases with decreasing in particle size. A. S. Azmi et al and S. Muhamad et al., 2006 conducted the experimental studies on Malaysian coal samples of particle size 1000µm and2000µm. They observed that the small particle size had a higher adsorption rate per unit mass of coal sample since the smaller particles will have a large surface area available for CO_2 gas adsorption.

Influence of particle size on CO_2 adsorption characteristics has shown a significant impact on Raniganj coal samples. The sorption experiment was done on three different particle sizes 150µm, 650 µm and 850µm. The adsorption capacities of three different particle sizes were shown in Fig 16. It is observed that the volume of gas adsorbed increased with increasing pressure in all the cases. However the adsorption capacity was maximum for 150 µm particle. The smaller particles will have a large surface area available for CO_2 gas adsorption (A. S. Azmi et al., 2006). Adsorption capacity decreased with increasing particle size.

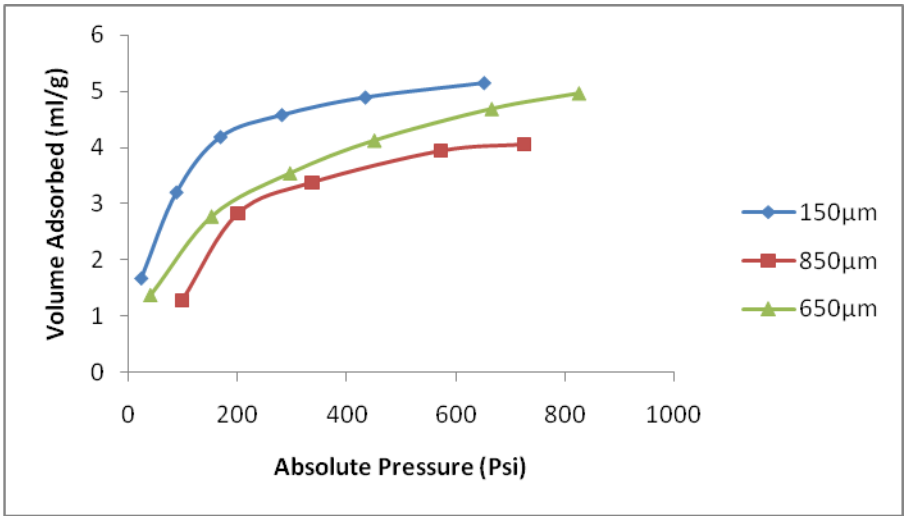

Fig16. Effect of particle size on CO_2 gas adsorption on coal S- 2

From the figure 16 it can be observe that the smaller particle size (150µm) adsorb more than the larger particle size (850µm). The adsorption capacities are 4.04ml/g and 5.15ml/g with respective particle sizes of 850 µm and 150 µm. From the results we concluded that the smaller particle size had a higher adsorption rate compare to the larger particle size. Because smaller particles will have a large surface area available for CO_2 sorption. Similar findings were observed with Malaysian coal (A.S.Azmi et al., 2006).

4.10. Effect of pH

The effect of pH on coal surface was studied by many researchers. K. Schroder et al., 2004 studied the effect of pH on adsorption of Malaysian coals of different pH range of 2.4, 6 and 12. The effect of coal surface pH was investigated by pre-soaking method. The coals were filtered and dried overnight in a vacuum oven at 50^0C. Then the samples were used to sorption tests. They were observed that both acid treatment to a pH 2.4 and a base treatment to a pH 12 result in an increase in sorption capacity compared to the untreated coal. Because these samples were all oven dried, moisture removal is to known to affect the porosity and transport properties of coal but the effects were very mild for high rank coals when the drying temperature below 100C(subberg et al., 1993). Experimental studies on effect of pH on Malaysian coals were carried out by A. S. Azmiet al and S.Yusup et al., 2006. The coal sample was treated with both acid and base medium. They observed that the adsorption capacities increased as compared to the untreated sample.

Effect of pH on CO_2 adsorption characteristics has shown a significant impact on Raniganj coal samples. The effect of pH on coal samples are shown in figure 17.

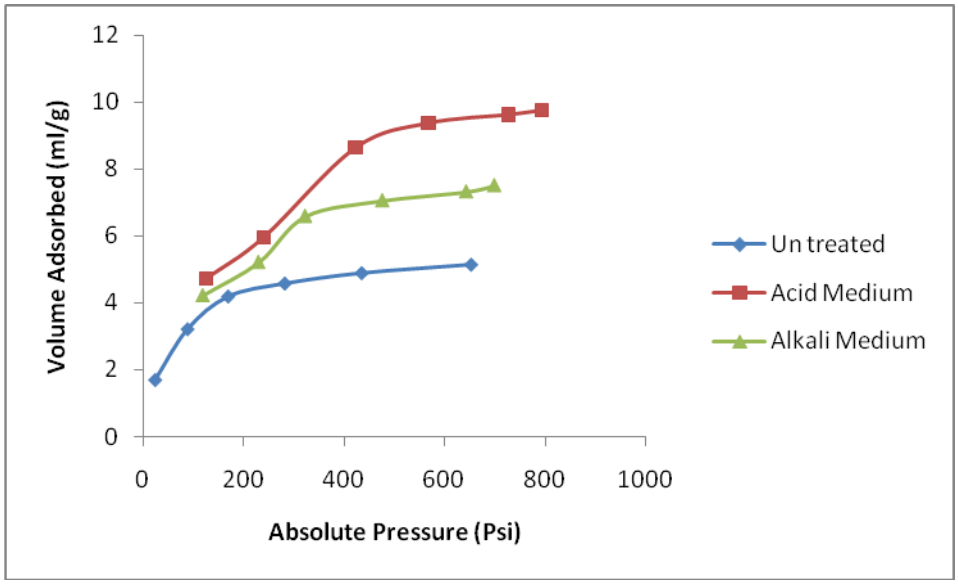

Fig17. Effect of pH on CO_2 gas adsorption on S-2

From the fig 17 it can be clearly seen that the sorption capacity increased with both acid and base medium than with the untreated sample. This is because some of the acid/alkali dissolves minerals present inside the coal during the treatment process which increases the available pore volume and thus increases the adsorption capacity as compared to the untreated sample (A.S.Azmi et al., 2006).

4.11. Effect of Temperature on adsorption capacity

Several researchers have studied the effect of temperature on the CO_2 sorption. K. Schroder et al., 2004, conducted laboratory experiments on Argonne Premium Upper coals from California. They studied the sorption characteristics at different temperatures of 22^0C, 30^0C, 40^0C and 55^0C. At the highest temperature 55^0C the amount of adsorption linearly increased up to 300 Psi. At 700Psi it has surpassed the amount of adsorption observed at lower temperature. This may be due to the change of the coal physical properties at higher temperatures. The amount of carbon dioxide adsorbed becomes linear in the high pressure region. This is because critical properties of carbon dioxide is 31.3^0C and 1070Psi (Weast et al., 1979). At temperature below the critical temperature the sorption capacity increased with increasing temperature (K.Schrooder et al., 2004). Their experimental results shows that the effect of temperature on sorption capacity of Argonne Premium Upper coals from California. With increasing temperature there is decrease in

the adsorption equilibrium capacity because higher temperatures increasingly favor the gas phase due to T*S entropy term in the free energy expression (K.Schrooder et al., 2004). A.S. Azmi et al., 2006, studied the influence of temperature on adsorption capacity on Malaysian coals. They conducted the experiments at different temperatures 22.4^0C, 30^0C, 40^0C, and 50^0C. They observed that by increasing temperature there is decrease in the sorption capacity of the Malaysian coal samples. This is because deeper beds have warmer coal seams which will adsorb less CO_2.

The temperature dependence of adsorption of gases has been well documented. According to various studies conducted in order to determine the effect of temperature on the adsorption of gases onto solids, the volume of gas adsorbed onto the solid decreases with increase in temperature at which the gas is adsorbed. It is because at higher temperatures the kinetic energy of the molecules of both the solid and the gas, given by the Boltzmann equation, is higher. This increase in kinetic energy caused corresponding increase in interaction between the molecules of the gas and the solid at the interface that lead to interaction. Thus resulted in reduction in the effective area of the solid available for adsorption. The comparison between the temperature plots of 31.1^0C, 40^0C and 50^0C of three samples S-1, S-2, and S-5 above their critical temperature are shown in Fig 18, 19, 20 respectively. Fig 21, 22 & 23 described the effect of temperature (below critical Temperature of the adsorbed gas) for samples 1, 2 & 5 respectively. In both the cases the adsorption behavior showed increasing trend for increasing pressure. However the adsorption capacity reduced with increasing pressure. Thus our reported results agreed to the findings of other researchers.

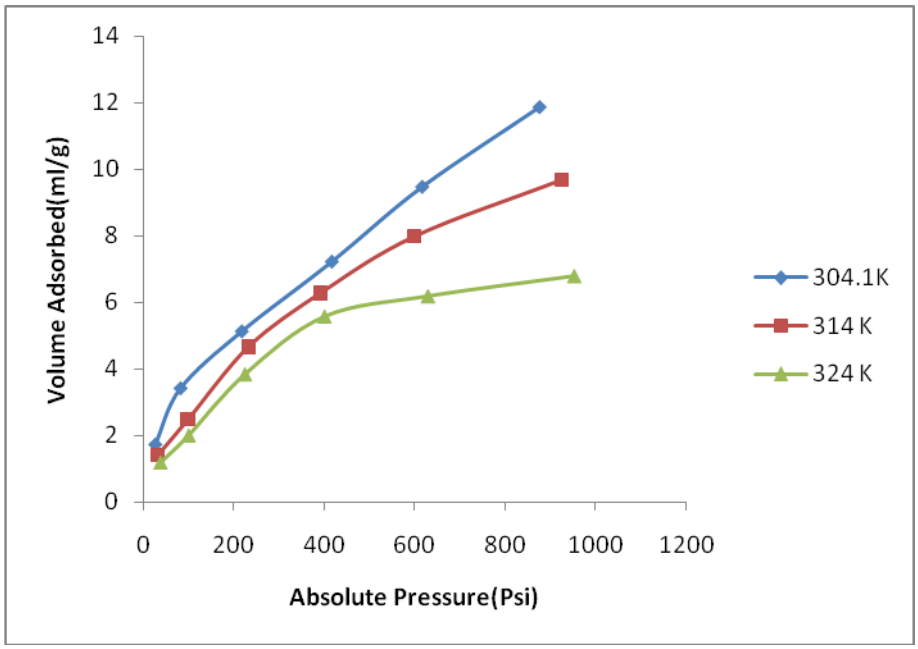

Fig 18. Influence of Temperature (above critical temp) S- 1

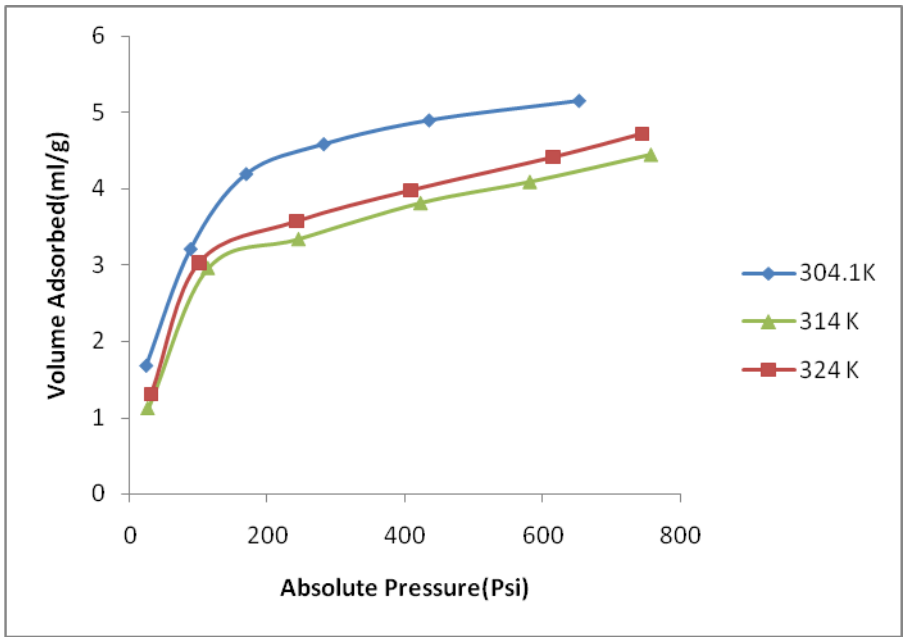

Fig 19. Influence of Temperature (above critical temp) S- 2

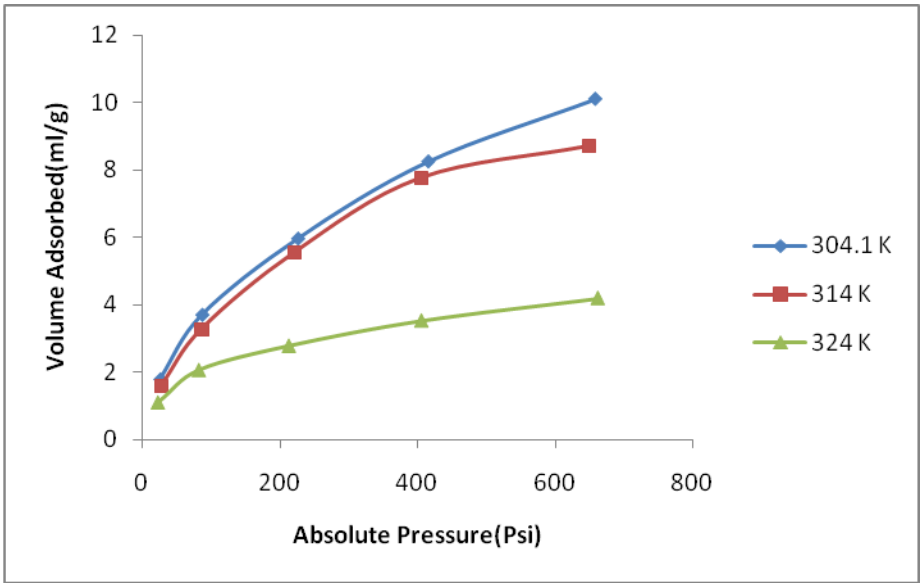

Fig20 Influence of Temperature (above critical temp) for S- 5

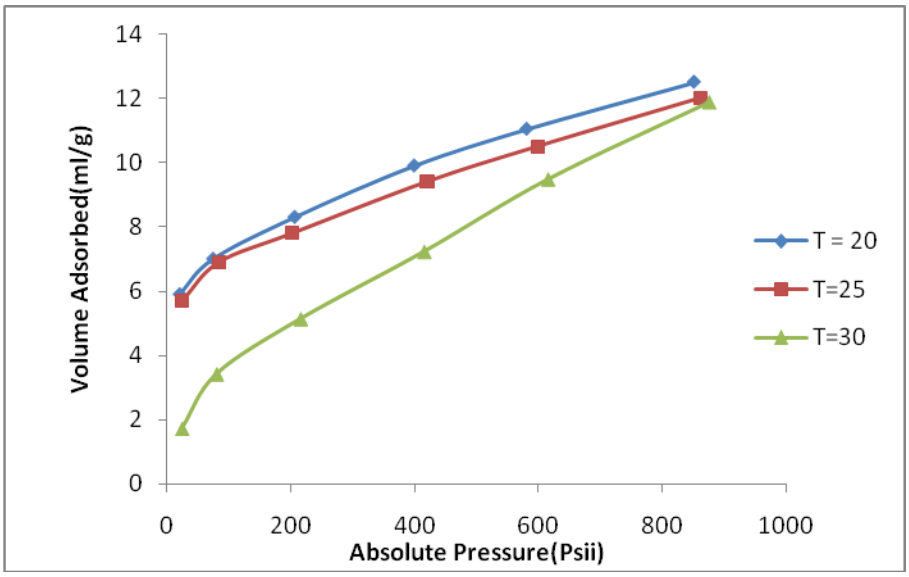

Fig21. Influence of temperature (below critical temperature) for S-1.

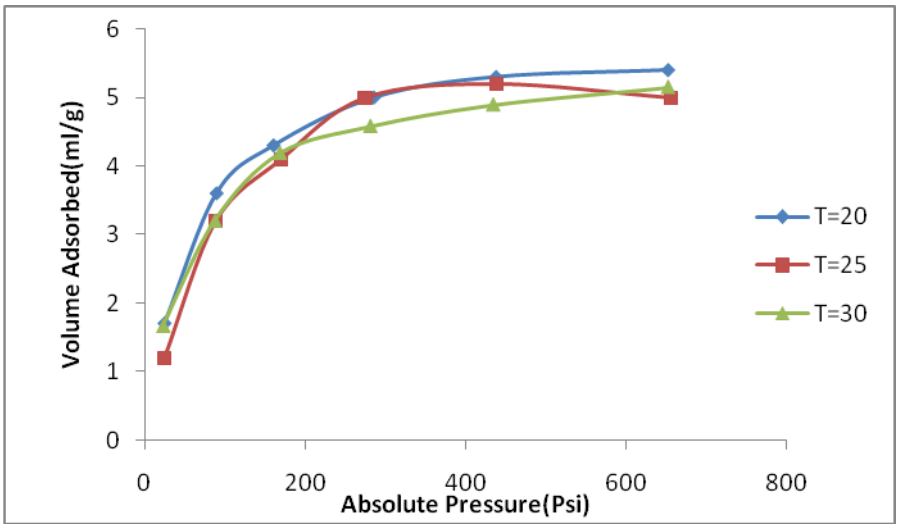

Fig22 Influence of Temperature (below critical temp) for S- 2.

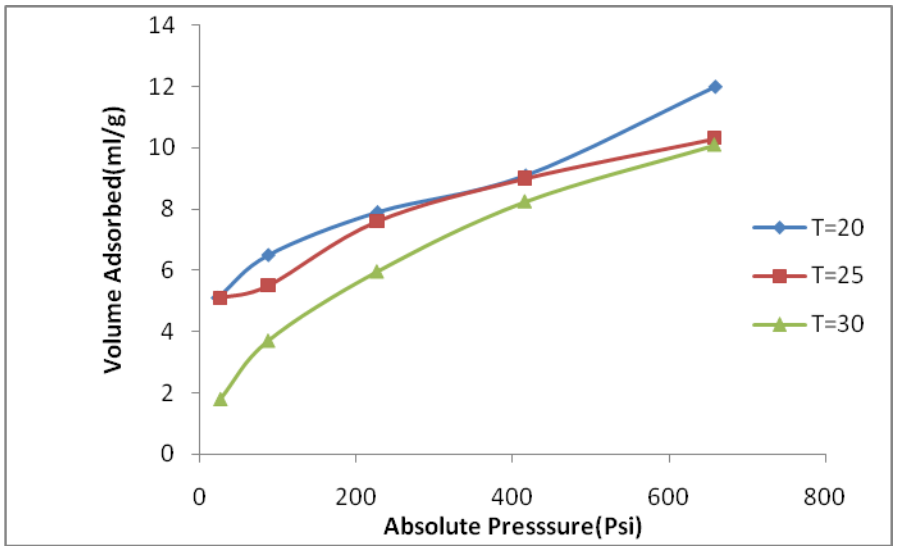

Fig23. Influence of Temperature (below critical Temp) for S- 5.

Characteristics curve is an important tool to predict the adsorption characteristics of a gas at different temperatures. It has important application in CBM production and CO_2 sequestration study where the actual gas adsorption data at different reservoir temperature is scarce.

To demonstrate the application of D-A equation to predict isotherms, the characteristic curve of CO_2 for the coal sample was plotted using experimental data at 30^0C. The D-A equation was then used to obtain the isotherm at 20^0C and 25^0C from the characteristic curve respectively. Initially, the saturated vapor pressure, Po, was estimated at the intended isotherm temperature. It

was assumed that the exponential term (n) in D-A equation, is independent of temperature. The following procedure was followed to obtain the isotherm at different temperatures:

- Initially the experimental data was used to plot, ln V versus A^n. A straight line plot was obtained and the equation of the plot was estimated.
- At a new temperature, the adsorption potential was estimated using the saturated Vapour pressure (P_o) values at that temperature.
- The values of A obtained was used to estimate A^n values using the same value of n.
- Thus corresponding to A^n values, lnV was estimated from the straight line equation outlined in step 1. Thus V could be estimated from lnV.

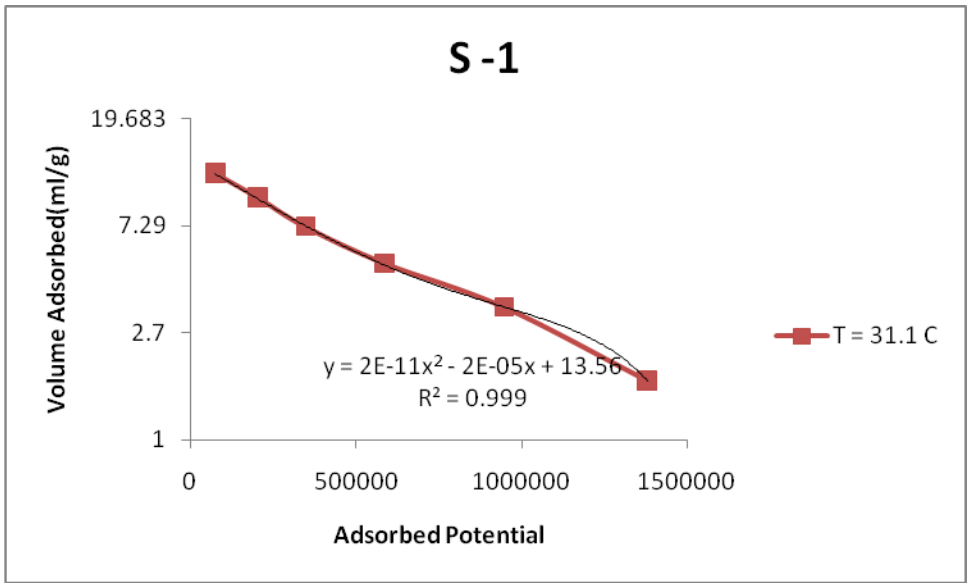

Fig24. Characterstic plot of S- 1

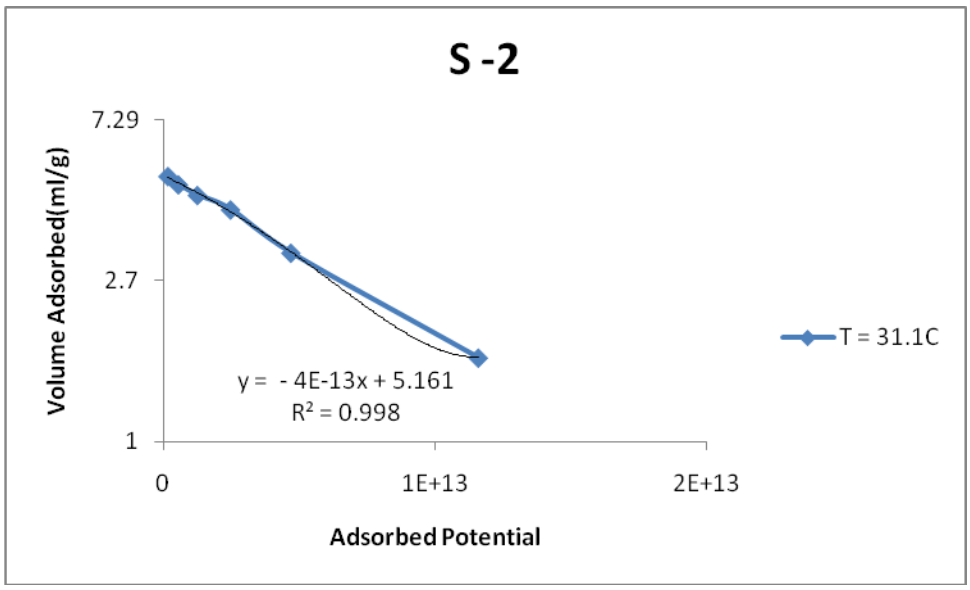

Fig25. Characterstic plot of S- 2

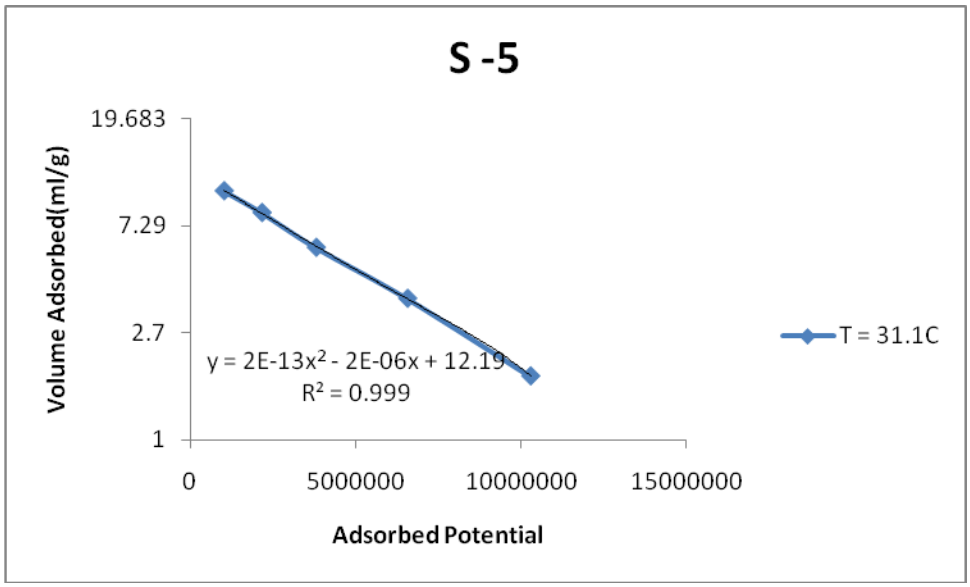

Fig26. Characterstic plot of S- 5

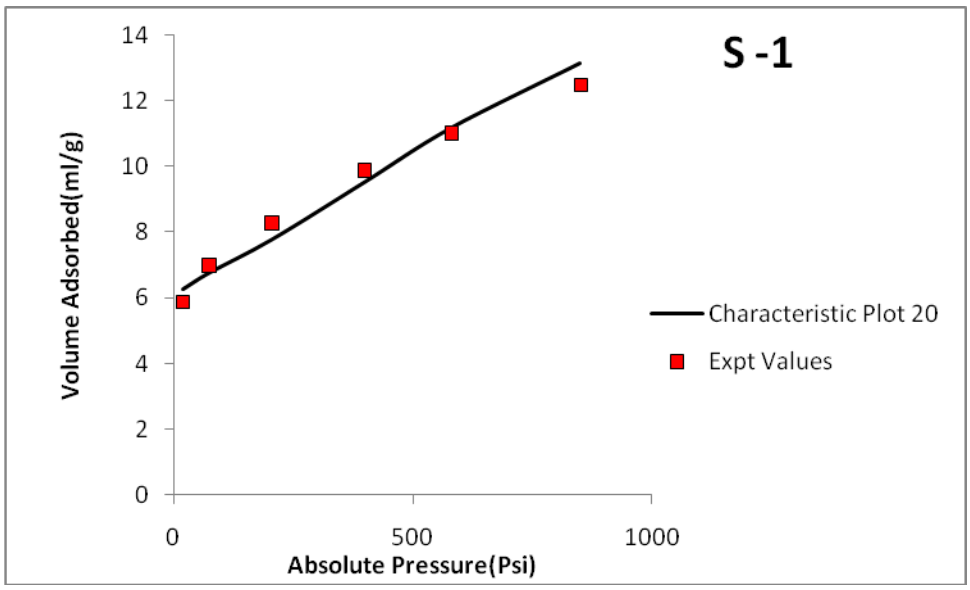

Fig27. Comparison of experimental values with predicted values for S- 1 at 20^0C

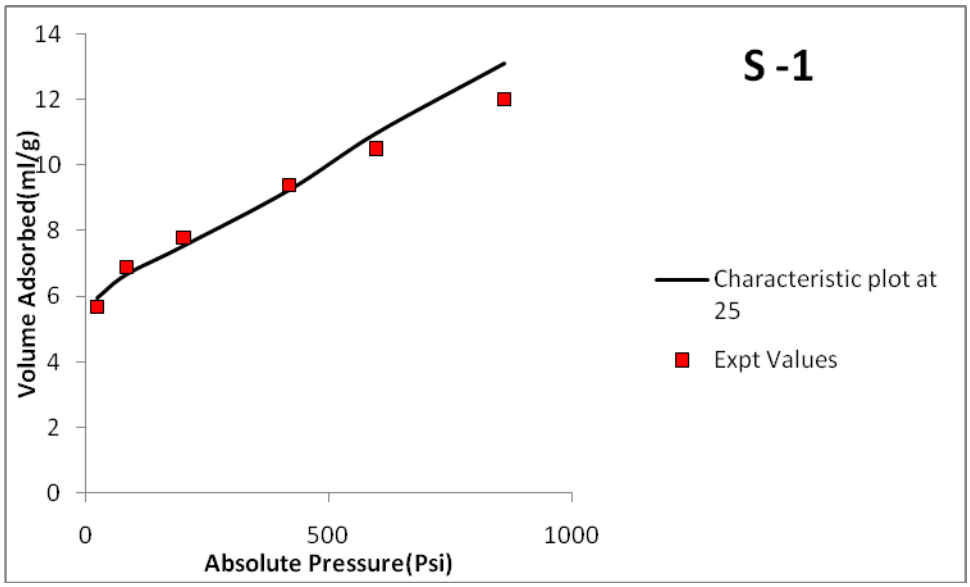

Fig28. Comparison of experimental values with predicted values for S-1 at 25^0C

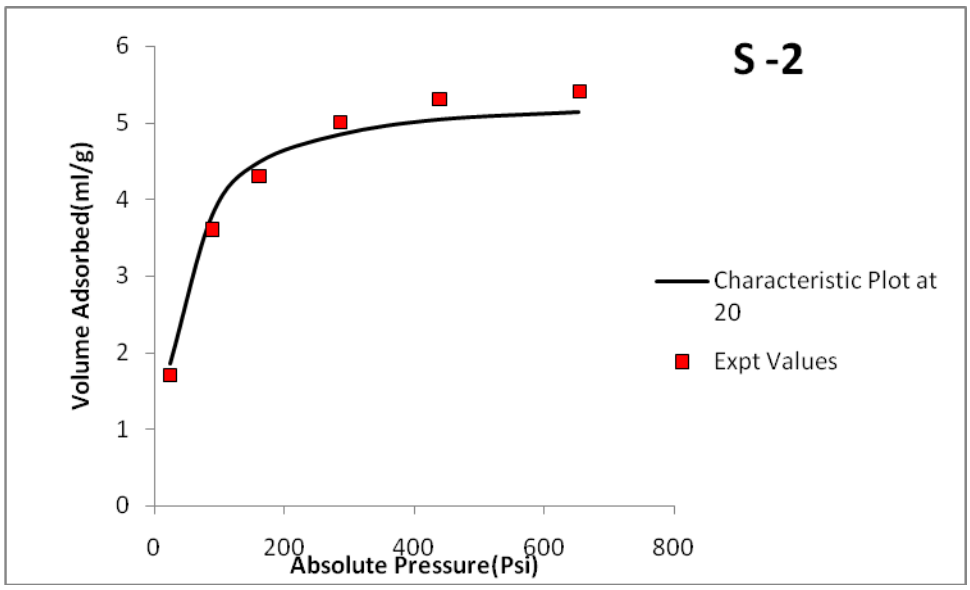

Fig29. Comparison of experimental values with predicted values for S- 2 at 20^0C

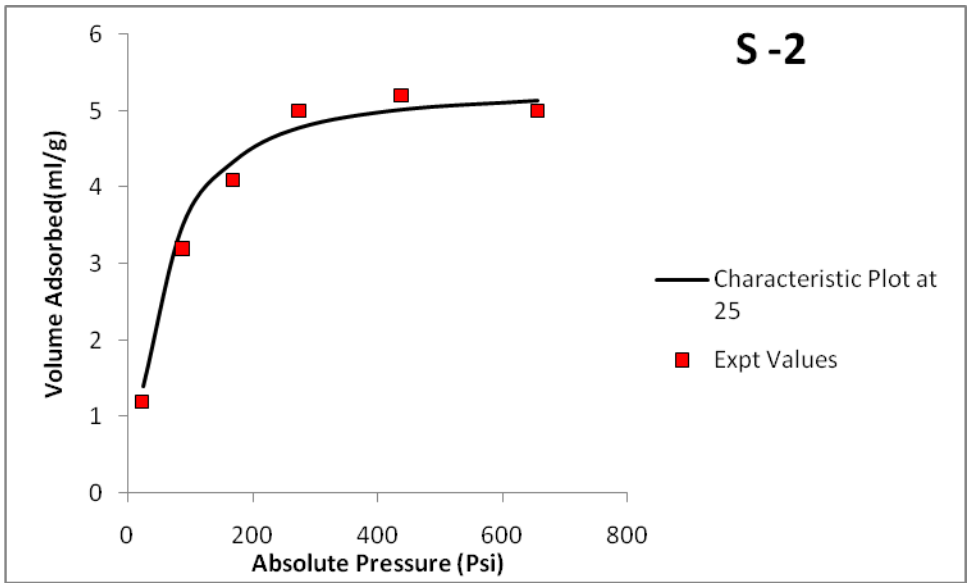

Fig30. Comparison of experimental values with predicted values for S- 2 at 25^0C

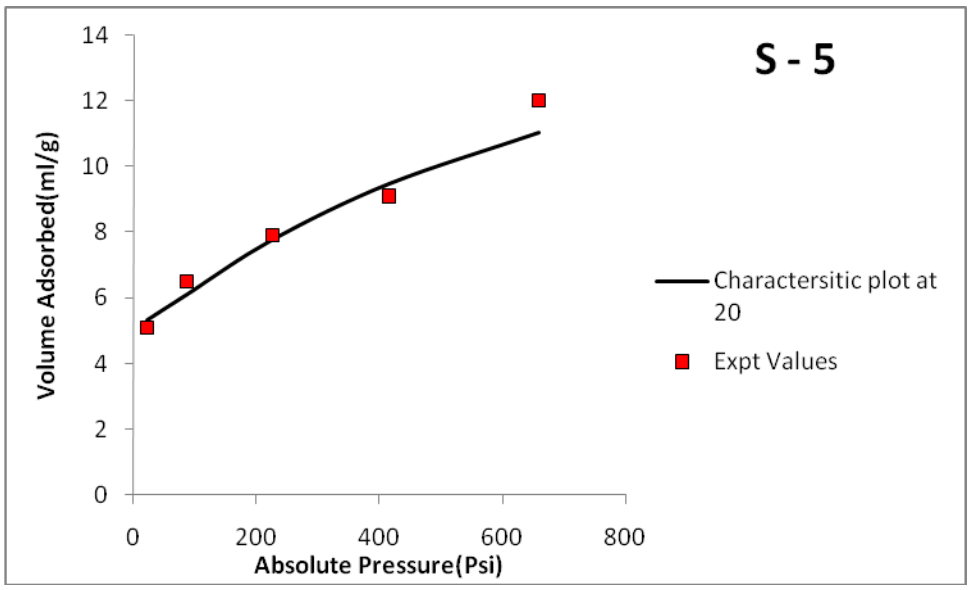

Fig31. Comparison of experimental values with predicted values for S- 5 at 20^0C

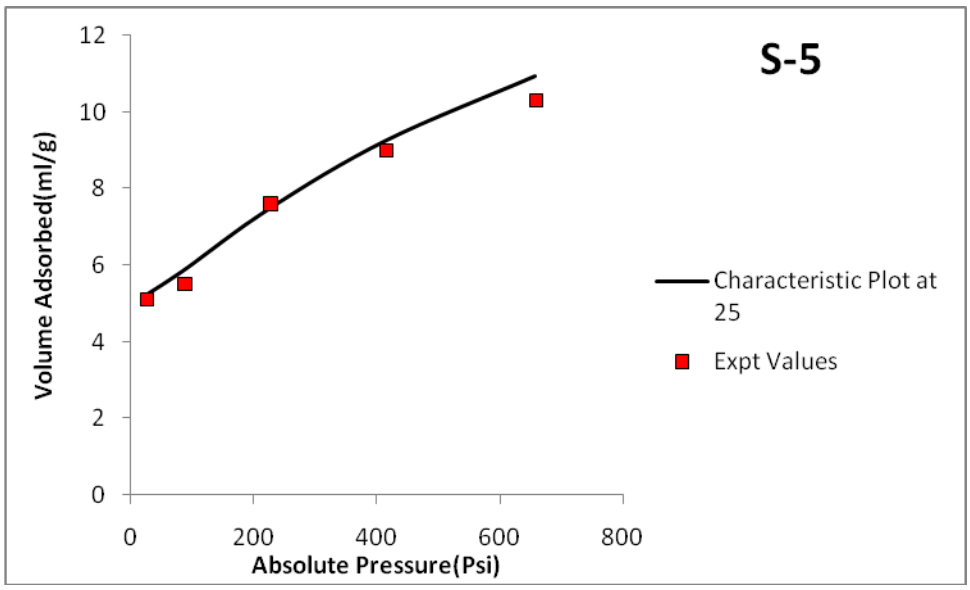

Fig32. Comparison of experimental values with predicted values for S-5 at 25^0C

The comparison of the experimental values with those obtained from the characteristic plot is shown in Fig 27, 29, & 31 at 20^oC. It can be seen that there is very little variation between the experimental and the theoretical values obtained from the characteristic plots. However little

deviation is observed at higher pressure only for all the samples. Similar results were reported at 25 ^{0}C for all samples. It can be thus concluded that this characteristic plot can be extensively used to predict the experimental data at new temperature provided it is below the critical temperature of the gas. With the given temperature gradient, it helps basically to evaluate the sequestration potential of a seam.

Chapter 5
Conclusions

Conclusion

- Carbon dioxide sorption studies were conducted on four samples obtained from Raniganj East CBM block of the Raniganj formation.
- Among all samples sample 1 had highest sorption capacity of 11.86ml/g (daf) at the pressure of 616Psi, and shows increasing trend.
- While sample 5 also showed higher sorption capacity 10.09ml/g (daf).
- By increasing seam depth sorption capacity shows an increasing trend.
- There has been no relation between adsorption capacity and other coal properties.
- The sorption capacity increases with increasing fixed carbon.
- The minimum desorption capacity was attained for sample 2, 1.29ml/g at the pressure of 22.361Psi.
- Hystresis was minimum for sample 1. While sample 3 and sample 5 showed maximum positive hysteresis. The hysteresis increases with increasing pressure initially and extended till 600Psi.
- The Langmuir isotherm model was failed to predict the data accurately. The D-A model gave an enough satisfactory representation suggesting that the pore filling model proposed by the Polanyi (Polanyi, M et al., 1914).
- From the absolute residual error Langmuir model has the highest residual error and D-A has lowest possible error. The %ARE values for Langmuir and BET are found to be comparatively very close.
- While for sample 2 and sample 3 % ARE values of both D-R and D-A models are relatively close to each other.
- As far as the effect of particle size on adsorption of CO_2 was concerned, the sorption capacity has been found to decrease with increase in particle size. This is in accordance

with previously conducted studies for various other coals. A significant jump in sorption capacity was observed from 850µm to 150µm.

- The pH has been found to affect adsorption in coal adversely at the extremes. The coal was found to have higher sorption at both acidic (high) and alkaline (low) pH levels.

- The effect of temperature on sorption exhibited a decreasing trend for an increasing temperature. This effect was also confirmed through theoretical studies using the characteristic plots derived from the D-A equation. There wasn't any change in this trend for the various samples with which the experiments were conducted. It was also confirmed that the adsorbed volumes derived from the characteristic plots were very much close to the experimental values with little deviations.

- With the temperature effects on adsorption that has been obtained for various seam depths a temperature gradient based adsorption capacity plot can also be deviced.

Chapter 6
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